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# CONTENTS.



## SERIES A. VOL. XCVI.

No. A 674.—August 1, 1919.

	PAGE
Zonal Harmonics of High Order in Terms of Bessel Functions. By John R. Airey, M.A., D.Sc. Communicated by Prof. J. W. Nicholson, F.R.S. ....	1
Atmospheric Stirring Measured by Precipitation. By Lewis F. Richardson. Communicated by Sir Napier Shaw, F.R.S. ....	9
Measurement of Water in Clouds. By L. F. Richardson. Communicated by Sir Napier Shaw, F.R.S. ....	19
Magnetic Storms of March 7-8 and August 15-16, 1918, and their Discussion. By C. Chree, Sc.D., LL.D., F.R.S. ....	32
On the Inter-crystalline Fracture of Metals under Prolonged Application of Stress (Preliminary Paper). By Walter Rosenhain, B.A., D.Sc., F.R.S., and Sydney L. Archbutt, F.I.C. (both of the National Physical Laboratory). (Plates 1-3.)	55
On the Determination of the Secular Acceleration of the Moon's Longitude from Modern Observations. By Ernest W. Brown, F.R.S. ....	69
On the Area of Surfaces. By Prof. W. H. Young, Sc.D., F.R.S. ....	71
On Change of the Independent Variables in a Multiple Integral. By Prof. W. H. Young, Sc.D., F.R.S. ....	82

No. A 675.—September 4, 1919.

On Certain Independent Factors in Mental Measurements. By J. C. Maxwell Garnett (late Fellow of Trinity College, Cambridge). Communicated by Prof. A. N. Whitehead, F.R.S. ....	91
Note on the Intensity Decrement in the Balmer Series. By T. R. Merton, D.Sc., and J. W. Nicholson, F.R.S. ....	112
Researches on the Chemistry of Coal. Part I.—The Action of Pyridine upon the Coal Substance. By William A. Bone, D.Sc., F.R.S., and Reginald J. Sarjant, M.Sc. ....	119
A Study of Catalytic Actions at Solid Surfaces. I.—Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel. By E. F. Armstrong, D.Sc., F.I.C., and T. P. Hilditch, D.Sc., F.I.C. Communicated by Prof. H. E. Armstrong, F.R.S. ....	137
The Value of the Rydberg Constant for Spectral Series. By W. E. Curtis, B.Sc., Demonstrator of Astrophysics at the Imperial College of Science, South Kensington. Communicated by Prof. A. Fowler, F.R.S. ....	147
Monoclinic Double Selenates of the Cobalt Group. By A. E. H. Tutton, D.Sc., M.A., F.R.S. ....	150

No. A 676.—October 9, 1919.

The Transparency of Biotite to Infra-red Radiations. By I. C. Martin, A.R.C.S., D.I.C., B.Sc., Lecturer in the Technical Optics Department, Imperial College of Science and Technology. Communicated by Prof. H. L. Callendar, F.R.S....	185
Experiments with Perforated Electrodes on the Nature of the Discharge in Gases at Low Pressures. By F. W. Aston, M.A., D.Sc., Clerk-Maxwell Student of the University of Cambridge. Communicated by C. T. R. Wilson, F.R.S. ....	200
De Saint-Venant Solution for the Flexure of Cantilevers of Cross-section in the form of Complete and Curtate Circular Sectors, and on the Influence of the Manner of Fixing the Built-in End of the Cantilever on its Deflection. By Mary Seegar, B.Sc., and Karl Pearson, F.R.S. ....	211
On the Relation between Wind and Distribution of Pressure. By Harold Jeffreys, M.A., D.Sc. Communicated by Sir Napier Shaw, F.R.S. ....	233
On a New Method of Driving off Poisonous Gases. By Mrs. Hertha Ayrton. Communicated by Prof. T. Maher, F.R.S. (Plate 4) .....	249

No. A 677.—November 1, 1919.

On the Colours of the Striae in Mica, and the Radiation from Lamellar Diffracting Boundaries. By Phanindra Nath Ghosh, M.A., Lecturer on Optics in the Calcutta University. Communicated by Dr. Gilbert T. Walker, C.S.I., Sc.D., F.R.S. ....	257
Diffusion of Light by Rain, Cloud, or Fog. By A. Mallock, F.R.S. ....	267
Bakerian Lecture: A Study of the Line Spectrum of Sodium as Excited by Fluorescence. By the Hon. R. J. Strutt, F.R.S., Imperial College, South Kensington. (Plate 5) .....	272
The Adsorption of Gases at Low and Moderate Concentrations. Part I.—Deduction of the Theoretical Adsorption Isostere and Isotherm. Part II.—Experimental Verification of the Form of the Theoretical Isosteres and Isotherms. By A. M. Williams, M.A., D.Sc., Chemistry Department, University of Edinburgh. Communicated by Prof. James Walker, F.R.S. ....	287
The Adsorption of Gases at Low and Moderate Concentrations. Part III.—Experimental Verification of the Constants in the Theoretical Adsorption Isostere. By A. M. Williams, M.A., D.Sc., Chemistry Department, University of Edinburgh. Communicated by Prof. James Walker, F.R.S. ....	298

No. A 678.—December 15, 1919.

Address of the President, Sir J. J. Thomson, O.M., at the Anniversary Meeting, December 1, 1919 .....	311
A Study of Catalytic Actions at Solid Surfaces. II.—The Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel. By Dr. E. F. Armstrong, F.I.C., and Dr. T. P. Hilditch, F.I.C. Communicated by Prof. H. E. Armstrong, F.R.S. ....	322
Tidal Friction in the Irish Sea. By G. I. Taylor, M.A. Communicated by Sir Napier Shaw, F.R.S. (Abstract) .....	330

A Linear Associative Algebra suitable for Electromagnetic Relations and the Theory of Relativity. By W. J. Johnston, M.A., Assistant Professor of Pure Mathematics in the University College of Wales, Aberystwyth. Communicated by Sir Joseph Larmor, F.R.S. ....	331
On Generalized Relativity in Connection with Mr. W. J. Johnston's Symbolic Calculus. By Sir Joseph Larmor, F.R.S., Cambridge .....	334

No. A 679.—January 2, 1920.

On the Variation with Frequency of the Conductivity and Dielectric Constant of Dielectrics for High-Frequency Oscillations. By G. E. Baird, D.Sc., D.Eng. Communicated by Prof. J. A. Fleming, F.R.S. ....	363
On the Secondary Spectrum of Hydrogen. By T. R. Merton, M.A., D.Sc. Communicated by Prof. A. Fowler, F.R.S. (Plates 6 and 7) .....	382
On the Spectra of Isotopes. By T. R. Merton, M.A., D.Sc. Communicated by Prof. A. Fowler, F.R.S. ....	388
The Scattering of X- and $\gamma$ -Rays by Rings of Electrons—A Crucial Test of the Electron Ring Theory of Atoms. By G. A. Schott, B.A., D.Sc., Professor of Applied Mathematics, University College of Wales, Aberystwyth. Communicated by Sir J. Larmor, F.R.S. ....	395
A Note on Dr. Chree's Recent Discussion of Two Magnetic Storms. By S. Chapman, M.A., D.Sc., F.R.S., Professor of Mathematics and Natural Philosophy in the University of Manchester .....	424
An Explanation of Criticisms on Dr. S. Chapman's Recent Paper, "An Outline of a Theory of Magnetic Storms." By C. Chree, Sc.D., LL.D., F.R.S. ....	426

No. A 680.—February 3, 1920.

The Measurement of Magnetic Susceptibilities of Low Order. By Ernest Wilson, M.Inst.C.E., M.I.E.E., Siemens Professor of Electrical Engineering in the University of London. Communicated by Prof. J. W. Nicholson, F.R.S. ....	429
On the Variations of Wave-length of the Oscillations Generated by Three-electrode Thermionic Tubes due to Changes in Filament Current, Plate Voltage, Grid Voltage or Coupling. By W. H. Eccles, D.Sc., and J. H. Vincent, M.A., D.Sc. Communicated by Prof. W. H. Bragg, C.B.E., F.R.S. ....	455
Equal Parallel Cylindrical Conductors in Electrical Problems. By F. J. W. Whipple, M.A. Communicated by Dr. C. Chree, F.R.S. ....	465

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OBITUARY NOTICES OF FELLOWS DECEASED.

Sir William Crookes (with portrait) .....	i
Sir Joseph Wilson Swan (with portrait) .....	ix
George Carey Foster .....	xv
Index .....	xix



# PROCEEDINGS OF THE ROYAL SOCIETY.

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## *SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.*

### *Zonal Harmonics of High Order in Terms of Bessel Functions.*

By JOHN R. AIREY, M.A., D.Sc.

(Communicated by Prof. J. W. Nicholson, F.R.S. Received January 13, 1919.)

The zonal harmonic  $P_n(\theta)$ , for large values of  $n$  and small values of  $\theta$ , is approximately given by the formula

$$P_n(\theta) = J_0(a\theta),$$

where  $a^2 = n(n+1)$ .

This result is easily derived from a consideration of Legendre's equation,

$$\frac{d^2u}{d\theta^2} + \cot \theta \cdot \frac{du}{d\theta} + n(n+1)u = 0, \quad u = P_n(\theta). \quad (1)$$

The first approximation of  $\cot \theta$  is  $1/\theta$ , and substituting this value in (1), the equation becomes

$$\frac{d^2u}{d\theta^2} + \frac{1}{\theta} \cdot \frac{du}{d\theta} + n(n+1)u = 0, \quad (2)$$

of which a solution is  $J_0(a\theta)$ , where  $a^2 = n(n+1)$ , a result similar to the one discovered by Mehler,\*

$$\lim_{n \rightarrow \infty} P_n\left(\cos \frac{x}{n}\right) = J_0(x). \quad (3)$$

The second solutions of (2), Bessel functions of the second kind or Neumann functions, do not appear in the expression for  $P_n(\theta)$ .

Macdonald† has given two formulæ for  $P_n(\theta)$  in terms of Bessel functions.

If  $x = (2n+1) \sin \frac{\theta}{2}$ ,

$$P_n(\theta) = J_0(x), \quad (4)$$

\* F. G. Mehler, 'Math. Annalen,' vol. 5, pp. 140-144 (1872).

† H. M. Macdonald, 'Proc. London Math. Soc.,' vol. 31 (Old Series), p. 269 (1899); *ibid.*, vol. 13 (New Series), pp. 320-1 (1914).



and

$$P_n(\theta) = J_0(x) + \sin^2 \frac{\theta}{2} \left\{ \frac{x}{6} J_3(x) - J_2(x) + \frac{1}{2x} J_1(x) \right\} \\ + \sin^4 \frac{\theta}{2} \left\{ \frac{x^3}{72} J_6(x) - \frac{11x}{30} J_5(x) + \frac{31}{12} J_4(x) - \frac{29}{6x} J_3(x) + \frac{9}{8x^3} J_2(x) \right\} \\ + \dots \dots \dots \quad (5)$$

whilst Lord Rayleigh\* obtained the result

$$P_n(\theta) = \left(1 + \frac{z^2}{12a^2}\right) J_0(z) + \frac{z}{6a^2} J_0'(z), \quad (6)$$

in which  $z = a\theta$  and  $a^2 = n(n+1)$ .

Further terms in the coefficients of  $J_0(z)$  and  $J_0'(z)$  can be found without difficulty by successive approximations. Equation (6) may be written

$$u = P_n(\theta) = \left(1 + \frac{\theta^2}{12}\right) J_0(a\theta) + \frac{\theta}{6a} J_0'(a\theta). \quad (7)$$

Consequently 
$$\frac{du}{d\theta} = a \left(1 + \frac{\theta^2}{12}\right) J_0'(a\theta), \quad (8)$$

and since

$$\cot \theta = \frac{1}{\theta} - \frac{\theta}{3} - \frac{\theta^3}{45} - \dots,$$

equation (1) becomes

$$\frac{d^2u}{d\theta^2} + \frac{1}{\theta} \cdot \frac{du}{d\theta} + a^2\theta = a \left(\frac{\theta}{3} + \frac{\theta^3}{45}\right) \left(1 + \frac{\theta^2}{12}\right) J_0'(a\theta) \\ = a \left(\frac{\theta}{3} + \frac{\theta^3}{20}\right) J_0'(a\theta). \quad (9)$$

Therefore 
$$\frac{d^2u}{dz^2} + \frac{1}{z} \cdot \frac{du}{dz} + u = \frac{1}{a^2} \left(\frac{z}{3} + \frac{z^3}{20a^2}\right) J_0'(z), \quad (10)$$

or, the dependent variable  $u$  being changed to  $vJ_0(z)$ ,

$$\frac{d^2v}{dz^2} + \frac{dv}{dz} \left(\frac{2J_0'}{J_0} + \frac{1}{z}\right) = \frac{1}{a^2} \left(\frac{z}{3} + \frac{z^3}{20a^2}\right) \frac{J_0'}{J_0}, \quad (11)$$

where the argument of the  $J$  functions is  $z$ .

Integrating (11), we find

$$\frac{dv}{dz} = \frac{1}{zJ_0^2} \left\{ A + \frac{1}{3a^2} \int z^3 J_0 J_0' dz + \frac{1}{20a^4} \int z^4 J_0 J_0' dz \right\}. \quad (12)$$

Now 
$$\int z^3 J_0 J_0' dz = -\frac{z^2}{2} J_1^2, \quad \int z^4 J_0 J_0' dz = -\frac{z^4}{6} (2J_1^2 - J_2^2).$$

It is easily seen that

$$\int z^4 J_0 J_1 dz = \int z^2 \cdot z^2 J_0 J_1 dz = \frac{z^4 J_1^2}{2} - \int z^3 J_1^2 dz.$$

\* Lord Rayleigh, 'Roy. Soc. Proc.', 1916, pp. 433-6.

But 
$$\int z^3 J_1^2 dz = \frac{z^4 J_1^2}{4} - \frac{1}{2} \int z^4 J_1 \left( \frac{J_1}{z} - J_2 \right) dz,$$

and therefore 
$$\begin{aligned} \int z^3 J_1^2 dz &= \frac{z^4 J_1^2}{6} + \frac{1}{3} \int z^4 J_1 J_2 dz \\ \int z^4 J_1 J_2 dz &= \int z^3 J_2 \cdot z J_1 dz = \int z^3 J_2 (z J_2' + 2 J_2) dz \\ &= \int (z^4 J_2 J_2' + 2 z^3 J_2^2) dz = \frac{1}{2} \int d(z^4 J_2^2) = \frac{z^4 J_2^2}{2}. \end{aligned}$$

Thus 
$$\int z^4 J_0 J_1 dz = \frac{z^4 J_1^2}{2} - \frac{z^4 J_1^2}{6} - \frac{1}{3} \cdot \frac{z^4 J_2^2}{2} = \frac{z^4}{6} (2 J_1^2 - J_2^2). \quad (13)$$

Hence 
$$\begin{aligned} \frac{dv}{dz} &= \frac{1}{z J_0^3} \left\{ A - \frac{z^2}{6 \alpha^2} J_1^2 - \frac{z^4}{120 \alpha^4} (2 J_1^2 - J_2^2) \right\}, \\ v &= B + A \int \frac{dz}{z J_0^3} - \frac{1}{6 \alpha^2} \int \frac{z J_1^2}{J_0^2} dz - \frac{1}{120 \alpha^4} \int \frac{z^3 (2 J_1^2 - J_2^2)}{J_0^2} dz. \end{aligned} \quad (14)$$

From the recurrence formula,  $J_2^2$  may be expressed in terms of  $J_0$  and  $J_1$ ; the integrals now occurring on the right-hand side of (14) are  $\int \frac{z J_1^2}{J_0^2} dz$  and  $\int \frac{z^3 J_1^2}{J_0^2} dz + 2 \int \frac{z^2 J_1}{J_0} dz$ .

Integrating  $\int \frac{z^3 J_1^2}{J_0^2} dz$  by parts, we get

$$\begin{aligned} \int \frac{z^3 J_1^2}{J_0^2} dz &= \int \frac{z^2 \cdot z J_1^2}{J_0^2} dz = z^2 \left( \frac{z J_1}{J_0} - \frac{z^2}{2} \right) - 2 \int z \left( \frac{z J_1}{J_0} - \frac{z^2}{2} \right) dz \\ &= \frac{z^3 J_1}{J_0} - \frac{z^4}{2} - 2 \int \frac{z^2 J_1}{J_0} dz + \frac{z^4}{4}, \end{aligned} \quad (15)$$

and therefore 
$$\int \frac{z^3 J_1^2}{J_0^2} dz + 2 \int \frac{z^2 J_1}{J_0} dz = \frac{z^3 J_1}{J_0} - \frac{z^4}{4}. \quad (16)$$

Since  $B = 1$  and  $A = 0$ , we find that

$$v = 1 - \frac{1}{6 \alpha^2} \left\{ \left( z - \frac{z}{5 \alpha^2} + \frac{z^3}{10 \alpha^2} \right) \frac{J_1}{J_0} - \left( \frac{z^2}{2} - \frac{z^3}{10 \alpha^2} + \frac{3 z^4}{80 \alpha^2} \right) \right\}, \quad (17)$$

and

$$\begin{aligned} u &= \left( 1 + \frac{z^2}{12 \alpha^2} + \frac{z^4}{160 \alpha^4} + \dots - \frac{z^2}{60 \alpha^4} \dots \right) J_0(z) \\ &\quad - \left( \frac{z}{6 \alpha^2} + \frac{z^3}{60 \alpha^4} + \dots - \frac{z}{30 \alpha^4} \dots \right) J_1(z) \\ &= \left( 1 + \frac{\theta^2}{12} + \frac{\theta^4}{160} + \dots - \frac{\theta^2}{60 \alpha^2} \dots \right) J_0(a\theta) \\ &\quad + \frac{\theta}{6 \alpha} \left( 1 + \frac{\theta^2}{10} + \dots - \frac{1}{5 \alpha^2} \dots \right) J_0'(a\theta). \end{aligned} \quad (18)$$

For the next approximation we obtain from (18) the value of  $du/d\theta$  as before. In this case

$$\frac{du}{d\theta} = \left\{ n \left( 1 + \frac{\theta^2}{12} + \frac{\theta^4}{160} \dots \right) + \frac{\theta^2}{60a} \right\} J_0' + \frac{\theta^3}{120} J_0.$$

When this is substituted, we find eventually the value of  $dv/dz$ , which now contains the term  $\int z^5 J_0^2 dz$  as well as integrals having the product  $J_0 J_0'$  in the integrand. But the former can be expressed in terms of the latter. Thus, integrating by parts,

$$\int z^5 J_0 J_0' dz = \frac{z^6 J_0^2}{2} - 3 \int z^4 J_0^2 dz,$$

$$\text{or, generally,} \quad \int z^{2m} J_0 J_0' dz = \frac{z^{2m+1} J_0^2}{2} - m \int z^{2m-1} J_0^2 dz. \quad (19)$$

Consequently, the problem of finding  $dv/dz$  depends upon the determination of the integral  $\int z^{2m} J_0 J_1 dz$ .

Now

$$\begin{aligned} \int z^{2m} J_{m-1} J_m dz &= \int z^{2m-1} J_m \cdot z J_{m-1} dz \\ &= \int z^{2m-1} J_m (z J_m' + m J_m) dz = \frac{z^{2m} J_m^2}{2}. \end{aligned} \quad (20)$$

$$\begin{aligned} \text{Also} \quad \int z^{2m} J_{p-1} J_p dz &= \int z^{2m-2p} z^{2p} J_{p-1} J_p dz \\ &= \frac{z^{2m}}{2} J_p^2 - (m-p) \int z^{2m-1} J_p^2 dz. \end{aligned} \quad (21)$$

$$\begin{aligned} \text{But} \quad \int z^{2m-1} J_p^2 dz &= \frac{z^{2m}}{2m} J_p^2 - \frac{1}{m} \int z^{2m} J_p J_p' dz \\ &= \frac{z^{2m}}{2m} J_p^2 - \frac{1}{m} \int z^{2m} J_p \left( \frac{p}{z} J_p - J_{p+1} \right) dz \\ &= \frac{z^{2m}}{2m} J_p^2 - \frac{p}{m} \int z^{2m-1} J_p^2 dz + \frac{1}{m} \int z^{2m} J_p J_{p+1} dz, \end{aligned}$$

and therefore

$$(m+p) \int z^{2m-1} J_p^2 dz = \frac{z^{2m}}{2} J_p^2 + \int z^{2m} J_p J_{p+1} dz, \quad (22)$$

or, combining the results in (21) and (22),

$$\begin{aligned} \int z^{2m} J_{p-1} J_p dz &= \frac{z^{2m}}{2} J_p^2 - \frac{(m-p)}{(m+p)} \left\{ \frac{z^{2m} J_p^2}{2} + \int z^{2m} J_p J_{p+1} dz \right\} \\ &= \frac{p}{m+p} \frac{z^{2m} J_p^2}{2} - \frac{m-p}{m+p} \int z^{2m} J_p J_{p+1} dz. \end{aligned} \quad (2)$$

Applying this formula, making  $p = 1, 2, 3, \dots$ , in succession, we obtain

$$\begin{aligned} \int z^{2m} J_0 J_1 dz &= \frac{z^{2m}}{2} J_1^2 - \frac{(m-1)}{(m+1)} \left[ \frac{z^{2m}}{2} J_1^2 + \int z^{2m} J_1 J_2 dz \right] \\ &= \frac{z^{2m}}{2} J_1^2 - \frac{(m-1)}{(m+1)} \left[ \frac{z^{2m}}{2} J_1^2 + \frac{z^{2m}}{2} J_2^2 \right. \\ &\quad \left. - \frac{(m-2)}{(m+2)} \left\{ \frac{z^{2m}}{2} J_2^2 + \int z^{2m} J_2 J_3 dz \right\} \right]. \quad (24) \end{aligned}$$

Finally, we reach the term  $\int z^{2m} J_{m-1} J_m dz$ . Thus

$$\begin{aligned} \int z^{2m} J_0 J_1 dz &= z^{2m} \left[ \frac{J_1^2}{m+1} - \frac{2(m-1)}{(m+1)(m+2)} J_2^2 + \frac{3(m-1)(m-2)}{(m+1)(m+2)(m+3)} J_3^2 - \dots \right] \\ &= \frac{z^{2m}}{m+1} \left[ J_1^2 + \sum_{r=1}^{r=m-1} \cos r\pi \frac{(r+1)(m-1)(m-2) \dots (m-r)}{(m+2)(m+3) \dots (m+r+1)} J_{r+1}^2 \right]. \quad (25) \end{aligned}$$

Similarly,

$$\begin{aligned} \int z^{2m} J_{p-1} J_p dz &= \frac{z^{2m}}{m+p} \left[ p J_p^2 + \sum_{r=1}^{r=m-p} \cos r\pi \frac{(r+p)(m-p)(m-p-1) \dots (m-p-r+1)}{(m+p+1)(m+p+2) \dots (m+p+r)} J_{r+p}^2 \right]. \quad (26) \end{aligned}$$

$$\begin{aligned} \int z^{2m-1} J_p^2 dz &= \frac{z^{2m}}{m+p} \left[ \frac{J_p^2}{2} - \frac{1}{m-p} \sum_{r=1}^{r=m-p} \cos r\pi \frac{(r+p)(m-p)(m-p-1) \dots (m-p-r+1)}{(m+p+1)(m+p+2) \dots (m+p+r)} J_{r+p}^2 \right]. \quad (27) \end{aligned}$$

In the final step of each approximation, to obtain the value of  $v$  it is necessary to evaluate integrals of the type  $\int \frac{z^{2m+1} J_1^2}{J_0^2} dz$  and  $\int \frac{z^{2m} J_1}{J_0} dz$ . These integrals occur under the form

$$\int \frac{z^{2m+1} J_1^2}{J_0^2} dz + 2m \int \frac{z^{2m} J_1}{J_0} dz. \quad m = 0, 1, 2, \dots$$

Integrating the first of these integrals by parts, and knowing that

$$\int \frac{z J_1^2}{J_0^2} dz = \frac{z J_1}{J_0} - \frac{z^2}{2},$$

we obtain the result

$$\int \frac{z^{2m+1} J_1^2}{J_0^2} dz = \frac{z^{2m+1} J_1}{J_0} + \frac{z^{2m+2}}{2m+2} - 2m \int \frac{z^{2m} J_1}{J_0} dz. \quad (28)$$

After further approximations, the expression for  $P_n(\theta)$  in terms of  $J_0(a\theta)$  and  $J_1(a\theta)$  is as follows:—

$$\begin{aligned} P_n(\theta) &= \left( \alpha_0 - \frac{\beta_0}{a^2} + \frac{\gamma_0}{a^4} - \frac{\delta_0}{a^6} + \dots \right) J_0(a\theta) \\ &\quad - \frac{\theta}{6a} \left( \alpha_1 - \frac{\beta_1}{a^2} + \frac{\gamma_1}{a^4} - \frac{\delta_1}{a^6} + \dots \right) J_1(a\theta), \quad (29) \end{aligned}$$

where  $\alpha_0 = 1 + \frac{\theta^2}{12} + \frac{\theta^4}{160} + \frac{61\theta^6}{120960} + \frac{1261\theta^8}{29030400} + \frac{79\theta^{10}}{20275000} + \dots$

$$\beta_0 = \frac{\theta^2}{60} + \frac{\theta^4}{420} + \frac{19\theta^6}{60480} + \dots,$$

$$\gamma_0 = \frac{2\theta^2}{315} + \frac{\theta^4}{560} + \dots, \quad \delta_0 = \frac{\theta^2}{210} + \dots,$$

$$\alpha_1 = 1 + \frac{\theta^2}{10} + \frac{31\theta^4}{3360} + \frac{17\theta^6}{18900} + \frac{9689\theta^8}{106444800} + \dots,$$

$$\beta_1 = \frac{1}{5} + \frac{4\theta^2}{105} + \frac{31\theta^4}{5040} + \dots,$$

$$\gamma_1 = \frac{8}{105} + \frac{\theta^2}{35} + \dots, \quad \delta_1 = \frac{2}{35} + \dots$$

To calculate  $P_n(\theta)$  to six places of decimals, when  $n$  is equal to or greater than 20, only  $\alpha_0$ ,  $\beta_0$ ,  $\alpha_1$ , and  $\beta_1$  need to be tabulated. The following tables have been constructed, giving these coefficients for each angle of the quadrant:—

$\theta^\circ$	$\alpha_0$	$\beta_0$	$\alpha_1$	$\beta_1$
0	1·0000000	0·00000	1·00000	0·2000
1	1·0000254	0·00000	1·00003	0·2000
2	1·0001016	0·00002	1·00012	0·2001
3	1·0002285	0·00004	1·00027	0·2001
4	1·0004063	0·00008	1·00049	0·2002
5	1·0006350	0·00012	1·00076	0·2003
6	1·0009148	0·00018	1·00110	0·2004
7	1·0012453	0·00024	1·00149	0·2006
8	1·0016270	0·00032	1·00195	0·2008
9	1·0020600	0·00041	1·00247	0·2010
10	1·0025448	0·00051	1·00305	0·2012
11	1·0030801	0·00062	1·00369	0·2014
12	1·0036675	0·00074	1·00440	0·2017
13	1·0043067	0·00086	1·00517	0·2020
14	1·0049978	0·00100	1·00601	0·2023
15	1·0057411	0·00115	1·00690	0·2026
16	1·0065368	0·00131	1·00786	0·2030
17	1·0073850	0·00148	1·00888	0·2034
18	1·0082860	0·00166	1·00996	0·2038
19	1·0092401	0·00186	1·01111	0·2043
20	1·0102476	0·00206	1·01232	0·2047
21	1·0113087	0·00228	1·01360	0·2052
22	1·0124237	0·00250	1·01495	0·2057
23	1·0135930	0·00275	1·01636	0·2063
24	1·0148168	0·00300	1·01784	0·2069
25	1·0160956	0·00326	1·01938	0·2075
26	1·0174297	0·00353	1·02099	0·2081
27	1·0188194	0·00382	1·02267	0·2088
28	1·0202652	0·00412	1·02442	0·2095
29	1·0217675	0·00443	1·02624	0·2102
30	1·0233287	0·00475	1·02813	0·2109
31	1·0249483	0·00509	1·03009	0·2117
32	1·0266179	0·00544	1·03212	0·2125
33	1·0283508	0·00580	1·03423	0·2133

$\theta^\circ$	$a_0$	$B_0$	$a_1$	$B_1$
34	1·0801425	0·00618	1·03640	0·3142
35	1·0819937	0·00657	1·03865	0·2151
36	1·0839049	0·00697	1·04097	0·2160
37	1·0858766	0·00739	1·04337	0·2170
38	1·0879095	0·00782	1·04585	0·2180
39	1·0400042	0·00827	1·04841	0·2191
40	1·0421618	0·00873	1·05104	0·2201
41	1·0443815	0·00920	1·05375	0·2212
42	1·0466655	0·00969	1·05655	0·2224
43	1·0490140	0·01020	1·05942	0·2236
44	1·0514277	0·01073	1·06238	0·2248
45	1·0539074	0·01127	1·06542	0·2261
46	1·0564539	0·01183	1·06855	0·2274
47	1·0590681	0·01240	1·07176	0·2287
48	1·0617507	0·01299	1·07506	0·2301
49	1·0645027	0·01360	1·07845	0·2316
50	1·0673250	0·01423	1·08193	0·2330
51	1·0702185	0·01488	1·08551	0·2346
52	1·0731842	0·01554	1·08918	0·2361
53	1·0762281	0·01623	1·09294	0·2377
54	1·0793362	0·01693	1·09680	0·2394
55	1·0825246	0·01766	1·10076	0·2411
56	1·0857894	0·01841	1·10482	0·2429
57	1·0891317	0·01918	1·10898	0·2448
58	1·0925528	0·01997	1·11324	0·2466
59	1·0960538	0·02078	1·11761	0·2486
60	1·0996361	0·02162	1·12209	0·2506
61	1·1033009	0·02248	1·12668	0·2526
62	1·1070496	0·02337	1·13138	0·2548
63	1·1108835	0·02428	1·13620	0·2569
64	1·1148042	0·02522	1·14114	0·2592
65	1·1188132	0·02619	1·14619	0·2615
66	1·1229117	0·02719	1·15136	0·2639
67	1·1271016	0·02821	1·15667	0·2664
68	1·1313845	0·02927	1·16209	0·2690
69	1·1357621	0·03036	1·16765	0·2716
70	1·1402361	0·03147	1·17334	0·2744
71	1·144808	0·0326	1·1792	0·277
72	1·149481	0·0338	1·1851	0·280
73	1·154256	0·0350	1·1913	0·283
74	1·159134	0·0363	1·1975	0·286
75	1·164119	0·0376	1·2039	0·289
76	1·169212	0·0389	1·2105	0·293
77	1·174416	0·0403	1·2172	0·296
78	1·179733	0·0417	1·2241	0·300
79	1·185165	0·0432	1·2312	0·303
80	1·190715	0·0447	1·2384	0·307
81	1·196386	0·0462	1·2457	0·311
82	1·202179	0·0478	1·2533	0·315
83	1·208096	0·0494	1·2610	0·319
84	1·214147	0·0511	1·2690	0·324
85	1·220327	0·0529	1·2771	0·328
86	1·226641	0·0547	1·2855	0·333
87	1·233094	0·0565	1·2940	0·338
88	1·239688	0·0584	1·3028	0·342
89	1·246427	0·0604	1·3117	0·348
90	1·253314	0·0625	1·3209	0·352

The formulæ and tables are of course especially useful when  $\theta$  is a small angle. They have been tested by computing  $P_n(\theta)$  for comparatively small

values of  $n$  and large values of  $\theta$ . Even in these extreme cases the results are correct to six places of decimals.

For the purposes of comparison, a short table of  $P_8(\theta)$  has been computed, giving in the second column the values of this function when the angle  $\theta$  is large, both  $\gamma_0$  and  $\gamma_1$  being required in these calculations. In the third column are the values calculated by Tallquist.\*

$P_8(\theta)$ .		
$\theta$ .	Calculated from (29).	Tallquist's values.
60° .....	-0.073638 (9)	-0.0736389
65° .....	-0.241143 (9)	-0.2411438
70° .....	-0.278015 (2)	-0.2780152
75° .....	-0.170219 (8)	-0.1702200
80° .....	+0.023307 (8)	+0.0233079
85° .....	+0.201746 (2)	+0.2017462
90° .....	+0.273437 (6)	+0.2734375

In the construction of this table  $J_0(a\theta)$  and  $J_1(a\theta)$  were calculated from Meissel's tables. When  $a\theta$  exceeds 15.5,  $J_0$  and  $J_1$  can be found to seven places of decimals from formulæ† derived from the addition theorem of these functions.

\* Tallquist, 'Acta Soc. Sc. Fennicæ' (Helsingfors), vol. 33, No. 4, pp. 1-8. Tables of  $P_n(\cos \theta)$  for  $n = 1, 2, 3 \dots 8$  to ten places of decimals for each degree of the quadrant; A. Lodge, Appendix to Lord Rayleigh's paper, "On the Acoustic Shadow of a Sphere," Tables of Zonal Harmonics for 5° intervals in the value of  $\theta$  from 0° to 90°, and  $n = 1, 2, 3 \dots 20$  to seven places of decimals, 'Phil. Trans.,' A, vol. 203, pp. 87-110 (1904).

† "The Addition Theorem of Bessel Functions of Zero and Unit Orders," 'Phil. Mag.,' vol. 36, September, 1918.

## *Atmospheric Stirring Measured by Precipitation.*

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Since on the average the water-content of the atmosphere is not increasing, the water which descends as precipitation must have been stirred up into the atmosphere. So we can compute the eddy-diffusivity from a knowledge of the mean precipitation and the mean vertical gradient of mass of water per mass of atmosphere.

Eddy-diffusivity is a statistical measure of the effect of circulatory motions which we cannot, or do not wish to, consider in detail. Since the mean values in this paper are taken over the whole globe, it follows (unfortunately) that even the largest circulatory motions between the pole and the equator are not considered in detail, and that their effect is included with the effect of the rising currents in cyclone or anti-cyclones, with cumulus-eddies, and with the smaller eddies due to dynamical instability, in producing the coefficients of eddy-diffusivity at which we shall arrive.

### *The General Equations for Stirring*

In Taylor's theory of atmospheric stirring,\* the density of the atmosphere and the stirring coefficient are treated as independent of height.

Under these restrictions he arrives at the equation

$$\frac{\partial \chi'}{\partial t} = K \frac{\partial^2 \chi'}{\partial h^2}, \quad (1)$$

where  $t$  is time,  $h$  is height,  $K$  is the eddy-diffusivity, and  $\chi'$  may be either the potential temperature, or the vapour pressure, or the horizontal velocity in a fixed azimuth.

The present paper deals with a range of height involving considerable variations of density and very large variations in the stirring, so that it is necessary to find an equation more general than (1). At the same time, it will be convenient to arrange to have a simple expression not only for  $\partial \chi' / \partial t$ , but also for the vertical flux.

Here we may usefully bear in mind the analogy with the conduction of heat in a solid. The total water in a portion of air, or the total entropy in it, are not altered by gently mixing it; and the same is true of its horizontal momentum in a fixed azimuth, if the mixing takes place without the action

\* 'Phil. Trans.,' A, vol. 215, p. 3 (1915).



of an external horizontal force in this azimuth. If, then,  $Z$  stands for any one of these three quantities or for any other quantity which

Has its total, for a definite portion of air, unchanged by the }  
internal rearrangement of that portion, (2)

Or by delay, (3)

then the rate of increase of the total  $Z$  in the portion must be due to  $Z$  flowing in over the sides. If we now take the portion to be a horizontal layer, and define the "upward flux" as

The ratio of amount of  $Z$  rising across a large horizontal }  
surface in unit time to the area of this surface, (4)

then rate of increase of  $Z$  in the layer  $dh$  must be

$$-\frac{\partial}{\partial h}(\text{upward flux}) dh. \quad (5)$$

If now  $\chi$ , without the dash, be defined as the amount of  $Z$  per unit mass of atmosphere, then

The amount of  $Z$  in  $dh$  is  $\chi \rho dh$ , (6)

so that 
$$\frac{\partial(\chi \rho)}{\partial t} = -\frac{\partial}{\partial h}(\text{upward flux}). \quad (7)$$

Now we can define a coefficient  $c$  such that

$$\text{Upward flux} = -c \frac{\partial \chi}{\partial h}, \quad (8)$$

and it will then be for observation to show whether  $c$  is a constant, as would be nice, or whether  $c$  depends on various factors, and in particular on  $\partial \chi / \partial h$ . But, if  $c$  is going to be useful, it must not have to be infinite when  $\partial \chi / \partial h = 0$ . Therefore we had better confine ourselves to conditions in which

The upward flux vanishes when  $\partial \chi / \partial h = 0$ . (9)

Now this implies that

$\chi$  must be unchanged by the simple transportation of air }  
to a different level. (10)

Now  $\chi$  is the total  $Z$  per unit mass of a definite portion of air. So, as the mass is unchanged by transport, (10) implies that

The total  $Z$  in a definite portion of air must be unchanged }  
by its removal to a different level. (11)

Fortunately, (11) is satisfied by the same three quantities which previously satisfied (2), so that (10) is satisfied when  $\chi$  is either mass of water per unit

of atmosphere, entropy per unit mass, or horizontal momentum per unit mass (better known as velocity), in a fixed azimuth. (11A)

If, in place of (8), we had made the flux proportional to  $c' \partial(\rho\chi)/\partial h$  where  $\rho\chi$  is the total amount of  $Z$  *per volume* instead of per mass of atmosphere then, to avoid an infinite value of  $c'$ , the flux would have to vanish when  $\partial(\rho\chi)/\partial h$  vanished. That would not be possible for the three given meanings of  $Z$ , because rising air changes its volume. So it appears that we had better keep to the definition (8).

Inserting (8) in (7), we have

$$\frac{\partial(\rho\chi)}{\partial t} = \frac{\partial}{\partial h} \left( c \frac{\partial\chi}{\partial h} \right). \quad (11B)$$

Now the left-hand side of (11B) is equal to  $\rho \partial\chi/\partial t + \chi \partial\rho/\partial t$ , and by the equation of continuity of mass,

$$\chi \partial\rho/\partial t = -\chi \operatorname{div} m, \quad (12)$$

where  $m$  is the vector momentum per unit volume.

Let us now suppose that any time change of mean density of the layer is either negligible, as will usually be the case, or else that it is separately accounted for. Then (11B) reduces to

$$\frac{\partial\chi}{\partial t} = \frac{\partial}{\partial h} \left( c \frac{\partial\chi}{\partial h} \right) = -g \frac{\partial}{\partial p} \left( c \frac{\partial\chi}{\partial h} \right), \quad (13)$$

since

$$dp = -g\rho dh. \quad (14)$$

Equation (13) is in effect identical with one mentioned by G. I. Taylor for the case of potential temperature.\*

On the right hand side of (13) there are two variables,  $p$  and  $h$ , both used as measures of height. It would be neater to use only one such measure. Therefore, as the  $dp$  is indispensable, let us replace the  $dh$  from (14). At the same time, in order to get a single constant, let us put  $g^2\rho c = \xi$ , then (13) becomes

$$\frac{\partial\chi}{\partial t} = \frac{\partial}{\partial p} \left( \xi \frac{\partial\chi}{\partial p} \right), \quad (15)$$

where  $\chi$  may have any one of the meanings (11A). Here  $\xi$  is left to be determined by observation, but we know beforehand that it is finite when  $\partial\chi/\partial p = 0$ .

The flux is given by (5), (8), and (14) that is to say, if  $\chi$  is the amount of  $Z$  per unit mass of atmosphere, then the amount of  $Z$  rising across a large horizontal surface per area per time is

$$+ \frac{\xi}{g} \frac{\partial\chi}{\partial p} \quad \text{or, equivalently,} \quad - \frac{\xi}{g^2\rho} \frac{\partial\chi}{\partial h}. \quad (16)$$

\* 'Roy. Soc. Proc.,' A, vol. 94, p. 140 (1918).

For the reasons already stated, it appears that it is the quantity  $\xi$  of equations (15) and (16) which should be observed, tabulated, and remembered, in preference to  $K$  of equation (1), which should be regarded only as a stepping stone whereby to reach  $\xi$ . The relation between  $K$  and  $\xi$  is found by equating the corresponding expressions for  $\partial\chi/\partial t$ , thus

$$K \frac{\partial^2 \chi}{\partial h^2} = \frac{\partial}{\partial p} \left( \xi \frac{\partial \chi}{\partial p} \right). \quad (17)$$

If  $\xi$  should happen to be independent of height, equation (17) simplifies to

$$\xi = g^2 \rho^2 K, \quad (18)$$

and in C.G.S. units the coefficient  $g^2 \rho^2$  is numerically equal to unity at an average height of 2 kilom. above mean sea level.\*

The physical dimensions of  $\xi$  are

$$(\text{Mass})^2, (\text{length})^{-2}, (\text{time})^{-5}. \quad (19)$$

*Note on Local Differences of Pressure in a Wind.*

G. I. Taylor† arrived at equation (1) by considering small portions of air which wandered from levels at which they were average samples of the atmosphere and arrived at a new level, there to remain by mixing with the surroundings. When referring to the diffusion of momentum, he provides a proof to show that the local differences of pressure, which Stanton's observations have shown to be of considerable magnitude, do not nevertheless on the average affect the momentum of a sample during its journey. The local differences of pressure, therefore, leave equation (1) unaltered both in form and in the value of the eddy viscosity. But Taylor regrets that his proof of this applies only to motion in two dimensions.

In the present paper the difficulty does not arise in the same form. No attempt is here made to show theoretically that  $c$  is numerically the same for all three meanings of  $\chi$ . That question is left to observation. Taylor, who originated this stimulating hypothesis, derived it from the consideration of "the mean vertical distance through which any portion of the atmosphere is raised or lowered while it forms part of an eddy till the time when it breaks off from it, and mixes with its surroundings." This distance would be difficult to define precisely, as mixing is a gradual process. Consequently, the hypothesis seems in need of empirical confirmation, and we come back again to observation.

What has been taken for granted in deriving equation (15), and has now

\* Computer's Handbook, diagram to face Part II, p. 55.

† 'Phil. Trans., A, vol. 215 (1915).

to be examined more closely, is that (2), (3), and (9) are satisfied when  $Z$  is momentum and  $\chi$  velocity, both in the same fixed horizontal direction. Now (3) is satisfied because the external forces on a horizontal lamina, due to local pressure differences, are normal to its surfaces and therefore cannot alter its horizontal momentum. Condition (2) is satisfied because forces between the parts cannot alter the momentum of the whole. In examining (9) we must distinguish between the mean velocity  $\bar{v}$ , which here plays the part of  $\chi$ , and  $v'$ , the deviation from the mean. The question is whether, if  $\partial\bar{v}/\partial h$  vanish at any level, can there be an upward flux of momentum across that level? In other words can there be an eddy-shearing-stress where there is no rate-of-mean-shear? The converse, of course, occurs where there are no eddies. Or to put the question over again in another way: imagine two adjacent horizontal layers each say 100 metres thick and having the same mean velocity; would it be possible for the faster moving portions to sort themselves out and to flock together into one layer, leaving the slower moving portions in the other? If molecules did that sort of thing, the occurrence would be one of the exceedingly rare exceptions to the second law of thermodynamics. We may reasonably expect that there is a corresponding law, on an enlarged scale so to speak, applicable to the statistical mechanics of eddy motion.

The only other possibility seems to be that portions of air should wander in from quite distant regions, giving a part of the vertical flux of momentum proportional to  $\partial^2\bar{v}/\partial h^2$  and a term in either (1) or (15) proportional to  $\partial^4\bar{v}/\partial h^4$ .

*Precipitation in the Kilometre next above the Ground.*

To come now from the general to the particular, let  $Z$  be mass of water, then  $\chi$  is mass of water per mass of atmosphere and, following Hertz, will be denoted by  $\mu$ . The mass of water in the form of vapour rising across one horizontal square centimetre per second is given by (16) on the average of a large horizontal area. And this must be equal to the average rainfall when the horizontal area is extended at that level to cover the whole globe. Accordingly we have

$$\frac{\xi}{g^2\rho} \frac{\partial\mu}{\partial h} = (\text{mean rate of precipitation}). \quad (20)$$

The observational data for insertion in this equation, to find  $\xi$ , have been extracted from Hann's '*Lehrbuch der Meteorologie*,' 3rd edition, to which the following paged references refer. According to Süring,  $\mu$  in free air at a height of 1 kilom. has an average equal to 76 per cent. of its value at sea-level (p. 233). The mean value of  $\mu$  at sea-level has been put equal to  $10.0 \times 10^{-3}$  which is its saturation value at  $14.3^\circ \text{C.}$  and 760 mm. Hg. (p. 221).

The temperature  $14.3^{\circ}\text{C}$ . is Dove's estimate of the mean temperature of the earth (p. 143). Consequently the average value of  $\partial\mu/\partial h$  in the first kilometre is  $-2.4 \times 10^{-8} \text{ cm.}^{-1}$ .

Next, the mean precipitation over the earth's surface is about  $90 \text{ cm. year}^{-1}$  according to Murray and Fritzsche (p. 363). For insertion in the preceding equations, this must be expressed as  $2.9 \times 10^{-6} \text{ grm. cm.}^{-2} \text{ sec.}^{-1}$ . This is the precipitation at the earth's surface. For comparison with the average value of  $\partial\mu/\partial h$  in the first kilometre, we should use the precipitation at a height of half a kilometre. Unfortunately, there is not much instrumental evidence concerning change of precipitation with height, as elevated rain-gauges are so much disturbed by wind (pp. 319 to 323). However, as rain-clouds have an average height (p. 280) well above the height we are considering, and as rain, though colder than the air through which it falls, can hardly condense any moisture on to itself, owing to the large latent heat of steam (p. 320), and as, further, streaks of rain, descending from clouds, are sometimes seen to disappear before reaching the earth (p. 303), the evidence, as far as it goes, indicates that the precipitation does not vary much up to a height of 500 metres. The mean density at this height is about  $1.2 \times 10^{-3} \text{ grm. cm.}^{-3}$ . Inserting the above mean values in the equation (20), we get  $\xi = 1.4 \times 10^6 \text{ cm.}^{-2} \text{ grm.}^2 \text{ sec.}^{-5}$  as a mean value for the whole earth at a height of half a kilometre. This measure of diffusion is in remarkable agreement with the mean deduced by Taylor\* from an analysis of temperatures on the Eiffel Tower; for Taylor found  $K = 10.0 \times 10^4$ , whence on the assumption that  $\xi$  did not vary with height, equation (18) would give  $\xi = g^2 \rho^2 \times 10^5 = 1.45 \times 10^6 \text{ C.G.S. units}$ . It is also of the same order as the values of  $g^2 \rho^2$  (viscosity)/(density) found by Akerblom, Hesselberg, and Taylor by analyses of the change of wind with height. Thus Taylor's hypothesis, that the same constant applies to both cases, is so far confirmed.

To revert to the exchanges of moisture, as the precipitation does not vary much with height between 500 metres and the ground, it follows from (20) that the product of  $\xi$  and  $\partial\mu/\rho\partial h$  must, on the average, be independent of height in this range. This statement will not apply to points within the vegetation film, because there transpiration will provide a source of  $\partial\mu/\partial t$  which has not been considered in forming the equations. Now, just above the vegetation film,  $-\partial\mu/\partial h$  is sometimes strikingly greater than the mean value  $+2.4 \times 10^{-8} \text{ cm.}^{-1}$ , which has been taken to hold at a height of 500 metres. For instance, Hill's results (p. 238) at Allahabad in latitude  $25\frac{1}{2}^{\circ}\text{N}$ . indicate an annual mean value of  $\partial\mu/\partial h = -66 \times 10^{-8} \text{ cm.}^{-1}$  between 1.2 metre and 14.0 metres above the ground. Again, in the metre

\* 'Roy. Soc. Proc.' A, vol. 94 (1918).

immediately above a grass moor, I have observed  $\partial\mu/\partial h = -1500 \times 10^{-8} \text{ cm.}^{-1}$  on an almost calm sunny March afternoon in latitude  $49^\circ \text{ N.}$ , when the surface soil was moist. This observation was taken with an aspirated wet-and-dry psychrometer. It is, of course, only an instance, perhaps an extreme one, but it suggests that the mean value of  $\xi$  in the first metre of height may be as low as 1000 or even less, which is interesting, because the values of  $\xi$  given by the observation of small floating objects to be published presently,\* also indicate that  $\xi$  is much less near the earth than at a height of 1 kilometre.

*Precipitation at a Height of 8.5 Kilometres.*

Next, it seems desirable to attempt to estimate the stirring coefficient  $\xi$  from the precipitation at great heights; for, although the estimate will inevitably be a very uncertain one, it offers the only indication available at the moment of the order of this important quantity. The precipitation at 8.5 kilom. probably does not consist of anything except the slow descent of the cloud itself. The evidence for this statement is that the size of the precipitating particles is observed to decrease with height, so that, at the highest mountain stations, at a height still much below 8.5 kilom., there is observed nothing larger than drizzle and fine powdery snow (p. 358).† Also that such a cloud-name as "cirro-nimbus" is not to be found in a list of cloud-forms (pp. 269 to 273). We can calculate the velocity  $V_H$  with which the cloud descends, by Stokes' formula, when we know the size of the ice particles. This has been measured by Pernter, by observation of coronæ, and he has found the diameter to range from  $0.5 \times 10^{-3} \text{ cm.}$  to  $2.0 \times 10^{-3} \text{ cm.}$  (p. 257). It will be convenient to make the following calculations separately for these two extreme diameters. Now Stokes' formula for the steady descent of a very small sphere is

$$V_H = -\frac{g}{18} \frac{(\text{Diameter})^2 \{(\text{density of sphere}) - (\text{density of fluid})\}}{(\text{Molecular viscosity of the fluid})}.$$

The molecular viscosity of the air at the temperature  $230^\circ \text{ A.}$ , which prevails at 8.5 kilom., is about  $1.48 \times 10^{-4} \text{ C.G.S.}$  and accordingly, for ice spheres of density 0.9, the terminal velocity is  $V_H = -0.33 \times 10^{-6} \times (\text{diameter})^2$ , so that, for Pernter's limiting diameters,  $V_H = -0.08 \text{ cm. sec.}^{-1}$  and  $-1.3 \text{ cm. sec.}^{-1}$ .

In comparison with these velocities due to gravity, those due to the electric charge and potential gradient are probably quite negligible, for at a height of 8.5 kilom. the mean potential gradient is probably only about

\* In "Weather Prediction by Numerical Process," Cambridge University Press.

† Paged references here are to Hann's 'Meteorologie,' 3rd edition.

0.04 volts per centimetre (p. 740), while the mobility of the large atmospheric ions has been found by Langevin and Pollock to be less than  $10^{-3}$  cm.<sup>2</sup> sec.<sup>-1</sup> volt<sup>-1</sup> (Kaye and Laby's tables), and the mobility of charged cloud particles would probably be even smaller.

On the other hand, the vertical velocity of the air may sometimes exceed the downward velocity of the particles through the air. The vertical velocity of the air, or more strictly its product with density, is here treated as part of the eddy motion, because its mean value over a level surface, including the whole globe, is zero. The air motion, therefore, does not affect our measure of precipitation, at least if horizontal variation of density can be neglected.

Suring's table for  $\mu$  stops at 8 kilom. Taking  $\mu$  as  $10.0 \times 10^{-3}$  at the earth's surface as before, it follows that mean  $\partial\mu/\partial h = -0.3 \times 10^{-8}$  cm.<sup>-1</sup> at 7.5 kilom. (p. 233). However, it is found later that we require  $\partial\mu/\partial h$  at the height of the centre of mass of cirrus, cirro-stratus and cirro-cumulus clouds, a height which is about 8.5 kilom. Making a short extrapolation from Suring's table, it is found that  $\partial\mu/\partial h = -0.2 \times 10^{-8}$  cm.<sup>-1</sup> at 8.5 kilom. Even if this figure were ten times in error, the stirring deduced from it would still be of interest.

The density of the air at 8.5 kilom. has a mean value of about  $0.50 \times 10^{-3}$  grm. cm.<sup>-3</sup>.\*

The mass of ice per unit, horizontal area of cirrus, cirro-stratus, and cumulus clouds has been estimated in another paper† as from

$$0.22 \times 10^{-3} \text{ to } 0.9 \times 10^{-3} \text{ grm.-cm.}^{-2},$$

according as the particle diameter was

$$0.5 \times 10^{-3} \text{ or } 2.0 \times 10^{-3} \text{ cm.}$$

these being the limits of the range observed by Pernter (Hann, p. 257). It will be convenient to follow these limits throughout the argument. The corresponding velocities of the particles in still air are, from Stokes' formula:—

$$V_H = -0.08 \text{ or } -1.3 \text{ cm.-sec.}^{-1}.$$

Now the cloud, when it occurs, often consists of thin layers separated by clear air. So, to find a mean mass of ice per volume, we must take, as the thickness of the layer, not the thickness of the cloud itself, but the mean range within which it occurs, equal to, say, twice the "probable variation" of its height. Now the extreme observed heights for these three kinds of cloud are 20 kilom. and 2 kilom. (p. 281). A quantity which varies at

\* Sir W. N. Shaw, 'Principia Atmospherica,' Table III.

† "Measurement of Water in Clouds," *infra*, p. 19.

random according to the law of error, as we may suppose the height of the cloud to do within this range, commonly has a "probable variation" equal to about 1/8 of the total range, which in this case is 18 Kilom. So we must imagine the ice as spread out in a total range of height of about 4.5 kilom. Thus, in the parts of the sky where these clouds are present, the mass of ice per volume would be respectively  $0.05 \times 10^{-8}$  and  $0.20 \times 10^{-8}$  gm. cm.<sup>-3</sup> for Pernter's limiting diameters of particles. Next we require the mean fraction of the sky of the whole globe, which is covered by cirrus, cirro-stratus, or cirro-cumulus. This fraction will be less than the mean cloudiness observed at mountain stations at heights of 2 kilom. or 3 kilom., for the latter includes also the alto-cumulus and alto-stratus, as well as some cumulus and special mountain clouds.

Some mean annual cloudinesses are set out below:—

Station.	Height.	Latitude.	Fractional cloudiness.	Reference to Hann.
	km.			
Theodul pass ...	3.3	46° N.	0.54	Page 293
Pic du Midi ...	2.9	42° N.	0.48	" 293
Blue Hill	—	42° N.	0.45	" 288
Mexican tableland	2.2	20.5° N.	0.48	" 294
Peruvian tableland	2.4	16° S.	0.37	" 292

On the average we shall probably not be far wrong if we take 0.3 of the globe's sky to be covered by cirrus, cirro-stratus, or cirro-cumulus. It follows then that the mean mass of ice per volume of atmosphere at a height of 8.5 kilom. is respectively

$$= 0.015 \times 10^{-8} \text{ and } 0.060 \times 10^{-8} \text{ gm. cm.}^{-3}$$

for Pernter's limiting diameters of particles. Inserting this, together with  $\rho = 0.50 \times 10^{-3}$  gm. cm.<sup>-3</sup>,  $\partial\mu/\partial h = 0.2 \times 10^{-8}$  cm.<sup>-1</sup>, and  $V_H$ , respectively  $-0.08$  cm. sec.<sup>-1</sup> and  $-1.3$  cm. sec.<sup>-1</sup>, in the formula which follows from equation (20), namely in

$$\xi = g^2 \rho \frac{\partial V_H}{\partial \mu / \partial h} \quad (21)$$

there results  $\xi = 3$  or  $180$  cm.<sup>-2</sup> gm.<sup>2</sup> sec.<sup>-5</sup> according as we take the smallest or the largest ice particles observed by Pernter; for  $\xi$  deduced in this way is proportional to the cube of the diameter of the ice particle. There have been many uncertainties in this calculation of  $\xi$  at 8.5 kilom., but even its upper limit,  $\xi = 180$ , is so very much smaller than the value  $\xi = 140000$  at a height of 0.5 kilom. as to make it certain that  $\xi$  diminishes greatly with



height in the upper part of the troposphere. In the stratosphere  $\xi$  must of course be so small as not to disturb the equality of temperature.

*Summary.*

The equation for diffusion is investigated in the general case in which the atmospheric density and the degree of turbulence must both be regarded as varying with height, and it is found that the stirring is best measured by the coefficient  $\xi$  in the equation

$$\frac{\partial \chi}{\partial t} = \frac{\partial}{\partial p} \left( \xi \frac{\partial \chi}{\partial p} \right)$$

in preference to  $K$  in  $\partial \chi / \partial t = K \partial^2 \chi / \partial h^2$ .

Here  $p$  is pressure,  $h$  the height, and  $\chi$  may be either entropy\* per unit mass, or mass of water per unit mass, or horizontal momentum per unit mass (better known as velocity) in a fixed azimuth.

From estimates of precipitation and of vertical gradient of water per mass of atmosphere, as means over the whole globe, it is found that  $\xi$  has the following mean values :—

Height.	
8500 metres .....	3 to 180 cm. <sup>-2</sup> gm. <sup>2</sup> sec. <sup>-6</sup>
500 „ .....	140000
0.5 „ .....	Possibly as low as 1000, or even less.

The value at 500 metres is in fair agreement with  $\xi$  as deduced from  $K$  calculated by Akerblom, Hesselberg, and Taylor for heights of a few hundred metres. The values of  $\xi$  at other levels are remarkably smaller.

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\* Mr. W. H. Dines points out in regard to entropy, that the statement (2) is only an approximation, for mixing depends ultimately on conduction or radiation, and these are irreversible processes which cause the total entropy to increase. However, when the initial difference of temperature between the ingredients is a very small fraction of the absolute temperature of the mixture, as in the case considered, the error committed must be very small. Potential temperature does not involve this error.

## *Measurement of Water in Clouds.*

By L. F. RICHARDSON.

(Communicated by Sir Napier Shaw, F.R.S.—Received February 26, 1919.)

Since the initial data on which a weather prediction is to be based must, to be adequate, include the water-content of the clouds; and since observations of this are scanty, it will be well to survey what can be done in this respect. Three types of cloud can be measured: I. Clouds into which an observer can enter. Several observers, notably Conrad and independently Wagner, have measured the water in clouds on mountains by drawing a measured volume of atmosphere over absorbing substances. The information is summarised in Hann's 'Meteorology,' 3rd edition, p. 306. II. Cloud through which the sun's outline can be seen and which also exhibit coronæ, as they often do. III. Uniform stratus, provided that some way can be found for measuring the size of the particles.

### II. *Thin Clouds.*

For clouds through which the sun can be seen shining, it is remarkable that the edge of the sun's disc, if observed through dark spectacles, almost invariably appears quite sharp, free from any blurring.

I have measured the diminution by clouds of the difference of brightness at the edge of the sun's disc by a special photometer, arranged as follows and drawn diagrammatically in fig. 1. An image of the sun is formed on a piece of stout white paper by means of a lens fitted with an iris diaphragm. The paper is illuminated from behind by an electric lamp, except for a small area which is rendered opaque and is brought into coincidence with the sun's image. Thus the lamp produces a constant difference of brightness, opposite in sign to that produced by the sun's image. By varying the iris diaphragm, or by the introduction of absorbing screens, the difference of brightness, due to the sun, is made to balance that due to the lamp. The instrument is standardised on the unclouded sun at the same zenith distance. To eliminate difficulties due to difference of colour between lamp and sun, the paper was observed through a piece of copper-ruby glass. The instrument could be made convenient and portable. Stray light scarcely disturbed the balance, provided the enclosure containing the lamp was black, except for its plane white translucent front.

For the interpretation of the readings we may reason as follows:—The difference of brightness between the sun and the adjoining sky must be due

to the light which comes straight through the cloud, and is independent of the general glow of scattered light which is superposed on the disc and its

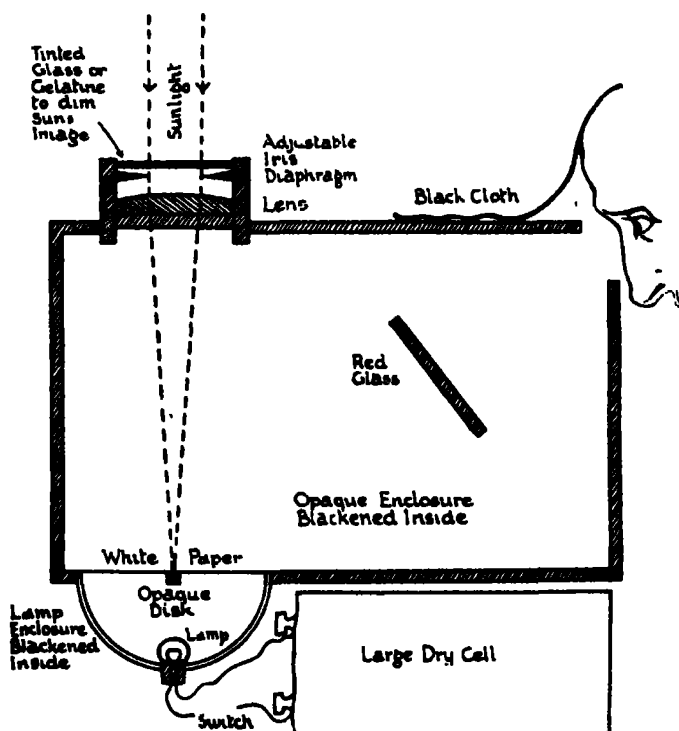


FIG. 1.—Diagram of Contrast Photometer.

surroundings alike. The fraction of the incident light which can come straight through must depend only on the size and number of the holes in the sieve, to which we may liken the cloud.

Thus, consider a portion of the beam of light  $1 \text{ cm.}^2$  in cross-section and of a length,  $dl$ , measured along the ray. Let there be a number,  $n$ , of particles per cubic centimetre, and let the particles be all of one size, and let  $A$  be the area of the diametral plane of a particle supposed spherical. Then the particles in  $dl$  remove a fraction  $An dl$  of the incident energy from the direct beam, by reflexion, refraction, or absorption. Diffraction may modify this result in the case of very small particles, but the ordinary cloud particle has a diameter some ten times longer than the wave-length of light, and for the present, diffraction has been neglected.

So if  $I$  be the difference of brightness at the sun's edge in the *direct* beam at any point

$$dI = -IAn dl. \quad (1)$$

If  $An$  be constant, we have on integrating

$$\log(I/I_0) = -Anl, \quad (2)$$

where  $l$  is the length of the ray passing through the cloud, and  $I_0$  is the initial difference of brightness.

Now, by the geometry of the sphere,

$$An = \frac{4}{3} \left\{ \frac{\text{volume of particles per volume of atmosphere}}{(\text{diameter of particle})} \right\}. \quad (3)$$

The product of the right side into  $l$  should therefore remain constant if  $I/I_0$  remains fixed. Now  $I/I_0$  is some sort of measure of the mental sensation of contrast of the object with its surroundings, which will reach a small, more or less fixed, value when  $l$  approaches the "distance of visibility" of a terrestrial object seen through a mist. Thus the above equation appears to be in harmony with the statement of W. Trabert\* that the distance of visibility is proportional to the diameter of the particle, for a fixed water-content presumably. The equation also harmonises with Aitken's observation† that the product of the distance of visibility into the number of dust particles per volume, is nearly constant at a fixed humidity, but increases if the particles grow in size by the condensation of vapour upon them. Our equation finds further support in the observations of Conrad and Wagner,‡ on the amount of water in certain clouds, when the data are compared with the diameters of the cloud particles measured by the same observers.§ For the mean of their observations may be summarised in the following formula:—

$$\frac{(\text{Distance of visibility}) \times (\text{volume of water per volume of cloud})}{(\text{Diameter of cloud particle})} = 2.9 \dots \quad (3a)$$

If we may insert this number 2.9 into formulæ (3) and (2), it would mean that Conrad and Wagner considered an object just invisible when  $I/I_0$ , the difference of brightness between it and its surroundings, fell to  $e^{-1 \times 2.9} = \frac{1}{17}$  of its value in absence of mist. This seems a not improbable ratio for a terrestrial object.

Now if the cloud is a horizontal layer it will be convenient to put  $dl = \sec \zeta \cdot dh$  where  $dh$  is the change of height corresponding to  $dl$ , and  $\zeta$  is the sun's zenith distance.

With this substitution equation (1) becomes

$$dI/I = -An \sec \zeta \cdot dh. \quad (4)$$

\* Hann's 'Meteorology,' 3rd edit., p. 360.

† Hann's 'Meteorology,' p. 16.

‡ Hann, p. 306.

§ Hann, p. 306.

On substituting the value of  $An$  from (3) and integrating across the vertical thickness of the cloud, (4) yields

$$\log \frac{I}{I_0} = -\frac{2}{3} \sec \zeta \int \frac{(\text{volume of particles per volume of air}) dh}{(\text{diameter of particle})}. \quad (5)$$

Now if the particles are all of one size, their diameter may be taken outside the integral in (5), which then comes out, no matter in what way the density of the cloud may vary with height, giving

$$\log_e \frac{I}{I_0} = -\frac{2}{3} \sec \zeta \frac{(\text{total volume of particles per horizontal area of cloud})}{(\text{diameter of particle})}. \quad (6)$$

If the particles are of water, not ice, this is the same as

$$\log_e \frac{I}{I_0} = -\frac{2}{3} \sec \zeta \times (\text{equivalent rainfall measured in diameters of a particle}), \quad (7)$$

which puts the result in its simplest form. Here  $I$  is the contrast of brightness at the sun's edge when seen through the cloud, and  $I_0$  is the contrast for the unclouded sun.

If the cloud is a mixture of particles of different sizes, represented by their diametral areas  $A_1, A_2, A_3, \dots$ , and if  $n_1, n_2, n_3, \dots$ , are the respective numbers of these particles per volume of atmosphere, then (1) becomes

$$dI = -I (A_1 n_1 + A_2 n_2 + A_3 n_3 + \dots) dl, \quad (8)$$

and the second member of (6) is made up of a corresponding series of terms, the total volume of each size of particles per horizontal area being divided by the diameter and the quotients being added.

It is conceivable that observations of coronæ, if sufficiently thorough, might enable us to disentangle the terms due to the different diameters. But in the present paper it is assumed that the droplets are all of one size.

My observational results are as follows:—

One noticed, by naked eye, a sensible dimming of the sunlight when  $I/I_0 = 0.7$ , as it is for the thinnest cirrus. At the other end of the scale, the sun's disk was just discernible through stratus, when  $I/I_0 = 1/10,000$ .

Thus, for the clouds cirrus, cirro-stratus, and cirro-cumulus, the average value of the volume of particles per horizontal area appears to be of the order of the radius of the particle. The range of values for the diameter found by Pernter, from observations of coronæ, was  $0.5 \times 10^{-3}$  cm. to  $2.0 \times 10^{-3}$  cm.\* Inserting these, together with the density of ice, we get for the mass of ice per horizontal square centimetre

$$0.22 \times 10^{-3} \text{ to } 0.9 \times 10^{-3} \text{ grm.-cm.}^{-2}.$$

\* Hann's 'Meteorology,' p. 257.

Description of cloud.	$-\frac{1}{2} \cos \zeta \cdot \log_e (I/I_0) =$ Volume of particles per horizontal area (diameter of particle)
Faintest cirrus. ....	0.07.
Very thin cirrus . . . . .	0.3, 0.8.
Ci or ci-stratus . . . . .	0.04.
Very thin ci-stratus . . . . .	} 0.06, 0.2, 0.8, 0.3, 0.5, 0.3, 0.8, 0.6, 0.4,
Ci-stratus, thin . . . . .	
Ci-stratus (typical ?) . . . .	} 0.4, 0.8.
Ci-cumulus . . . . .	0.6.
Ci-cumulus + ci-stratus . . . .	0.8, 0.9, 2.1.
Alto-cumulus . . . . .	0.5.
Stratus, sun much dimmed, but	} 2.5.
still obvious at $\zeta = 45^\circ$	
Stratus, sun's disk just visible	4.1.
at $\zeta = 49^\circ$	

As a caution, it must again be noted that diffraction ought to be considered before this result is relied upon.

### III. Thick Stratus.

For uniform stratus it is customary to make a very rough eye estimate of the water-content expressed in such words as "thin, heavy, dark, ugly, lowering." Can photometric measurements yield a corresponding numerical quantity?

The apparatus which I have used for this purpose was made as follows: A wedge of blotting paper was fixed inside a blackened cigar box, where it could be observed through a small hole covered with red gelatine. The two sides of the wedge were illuminated by the light passing through two adjustable iris diaphragms. The diaphragms were covered by pieces of white paper. One piece of paper was illuminated by a small electric lamp, which served as an intermediate standard. The other piece of paper was illuminated either by the unclouded sun, which served as the absolute standard, or alternatively by a small definite solid angle of stratus cloud. The iris diaphragms were adjusted until the two sides of the wedge appeared equally bright. In this way the light from a small solid angle of sky was found. In calculating the light from the whole sky, there is a trap of which it is well to beware. The solid angle of a hemisphere is  $2\pi$ , but the light falling on a horizontal area from a uniformly bright sky is only  $\pi$ , not  $2\pi$  times the light from unit solid angle, on account of obliquity. For if  $\zeta$  is the zenith distance, the solid angle between  $\zeta$  and  $\zeta + d\zeta$  is  $2\pi \sin \zeta \cdot d\zeta$ ; and the projection of the horizontal area normal to the same

direction is proportional to  $\cos \zeta$ . So the light falling on the horizontal area is proportional to the brightness of the sky at  $\zeta$  multiplied by  $2\pi \sin \zeta \cos \zeta \cdot d\zeta$ , which is equal to  $-\frac{1}{2}\pi d(\cos 2\zeta)$ , the integral of which from  $\zeta = 0$  to  $\zeta = \frac{1}{2}\pi$  is  $\pi$ .

This also shows that a correct way to average the observations is to plot them as a function of  $\cos 2\zeta$  and to find the area under the curve, for this procedure gives proper weight to the different zones. The light falling on an area of ground must be equal to the light leaving an equal area of cloud, if the cloud is uniformly bright and if the scattering of the intervening air be neglected. Again, neglecting scattering, the light falling on the upper surface of the cloud is proportional to the cosine of the sun's zenith distance, which can be found from the date and the time. [Scattering can be allowed for by reference to the Tables of L. V. King,\* based on the Smithsonian observations.] In this way I found that a strato-nimbus cloud of ordinary appearance transmitted a quarter of the red light falling on its upper surface.

A preliminary interpretation of such a result may be developed from Schuster's theory of "Radiation through a Foggy Atmosphere."†

Following Schuster, let us divide directions into two large groups, in our case by a horizontal plane.

Let  $E$  be the sum of all radiation which has a downward component.

$E'$  the sum of all radiation which has an upward component.

Let  $dh$ , as usual, be an element of length drawn vertically upward. As a rough allowance for the variety of directions of the rays, we may put the path of the ray as  $\sqrt{2}dh$ , corresponding to a slope of  $45^\circ$ . Then if  $C$  is the fraction of the radiation which has its vertical component reversed in sign by the scattering in unit length of ray, we have

$$-\frac{dE'}{\sqrt{2} \cdot dh} = C \{E - E'\}, \quad (9)$$

$$\frac{dE}{\sqrt{2} \cdot dh} = C \{E - E'\}, \quad (10)$$

$$\text{whence} \quad \frac{d(E - E')}{dh} = 0 \quad (11)$$

$$\text{and} \quad \frac{d}{\sqrt{2} \cdot dh} (E + E') = 2C(E - E'). \quad (12)$$

Now, at the lower surface of the cloud, the upward radiation bears to the downward radiation a ratio equal to the reflectivity of the earth, vegetation,

\* 'Phil. Trans.,' A, 1913.

† 'Astrophys. Jour.,' vol. 21, No. 1, Jan., 1905.

or sea. Putting  $B$  for this reflectivity, and letting subscript  $i$  distinguish values at lower surface of the cloud, we have

$$BE_i = E'_i. \quad (13)$$

$$E_i + E'_i = E_i(1+B); \quad E_i - E'_i = E_i(1-B). \quad (14, 15)$$

But, by (11),  $E - E'$  is independent of height, so that in general

$$E - E' = E_i(1-B), \quad (16)$$

$$E + E' = 2E - (E - E') = 2E - E_i(1-B). \quad (17)$$

Consequently equation (12) becomes, since  $E_i$  does not depend on  $h$ ,

$$\frac{d}{\sqrt{2}dh} 2E = 2CE_i(1-B). \quad (18)$$

Integrating upwards from the lower surface,

$$E = \sqrt{2} \cdot E_i(1-B) \int_i C dh + \text{const.} \quad (19)$$

and the constant of integration must be

$$E_i. \quad (20)$$

So that at the top of the cloud, denoted by a subscript zero,

$$E_0 = \sqrt{2} \cdot E_i \left\{ 1 + (1-B) \int_i^0 C dh \right\}. \quad (21)$$

Again, at the top of the cloud the downward component of direct sunlight is

$$E_0 = S \cos \zeta, \quad (22)$$

where  $\zeta$  is the sun's zenith distance and  $S$  the intensity for a zenith sun.

$$\text{Therefore} \quad \frac{S \cos \zeta}{E_i} = \sqrt{2} \left\{ 1 + (1-B) \int_i^0 C dh \right\}. \quad (23)$$

Now  $E_i/S \cos \zeta$  is the fraction of the incident light which is transmitted by the stratus cloud, and is a quantity which can be observed.

Another quantity required for equation (23) is  $B$ , the reflectivity of the earth's surface. This has been observed by a simple photometer consisting of a white wedge in a black box, the sides of the wedge being illuminated by lights from diametrically opposite directions, admitted to the box through adjustable iris diaphragms, one opening to the earth, the other to uniform stratus. In this way I found, for directions near the zenith and nadir, the following ratios of brightness of ground, to brightness of stratus, for red light. Fresh snow, 0.65; dry chalk in Eastern Champagne, France, 0.2; sea-sand, damp but not glistening, Seaview, Isle of Wight, 0.13; grass, 0.15, 0.06; sea, grey green, between Portsmouth and the Isle of Wight, 0.06; stubble after hay harvest, 0.04; green oats on chalk, 0.03; loam, damp dark brown, 0.03; dark



green bushes, 0.01. Except in the cases of snow and water these numbers may be taken as first approximations to  $B$ . For snow and water the reflectivity depends notably on direction, and the instrument which has just been described does not enable us to deal effectively with that variation, because it contains no reference standard.

Of the quantities in equation (23) it remains to consider  $\int_0^1 C dh$  where  $C$  is the fraction of the radiation which has its vertical component reversed in sign by the scattering in unit length of ray, and where the integration is taken across the vertical thickness of the cloud.

To find  $C$  we need in the first place the fraction of direct sunlight turned back by a single drop of water. As previously we have only considered two groups of directions called "upwards" and "downwards" for short, so here we only need a division into "forwards" and "backwards," the division being made by a plane through the drop at right angles to the incident sunlight. However, it has not been found possible to obtain a convincing answer to the question: what fraction of the light is turned backwards? without exploring the distribution of light in detail. This is not to be regretted, for the detail will be required in any future thorough treatment of the problem, in which directions are divided into infinitesimal groups instead of into two hemispheres.

It will be convenient to express the intensity of the scattered radiation by a quantity which depends only on the angle between the incident and the scattered radiation, and which has unity for its mean value. Such a quantity is  $\psi$  defined by

$$\psi = \frac{(\text{candle-power of drop in any direction})}{(\text{mean spherical candle-power of drop})} \quad (24)$$

Now  $\psi$  is independent of the unit chosen for candle-power, and therefore we may, if we like, interpret candle-power to mean  $r^2$  times the energy per second falling normally on unit area placed at a great distance,  $r$ , from the drop. Then, since the area of a sphere of this radius is  $4\pi r^2$ , it follows that the mean spherical candle-power is equal to the whole energy falling on this large sphere, divided by  $4\pi$ . And since the drop is transparent, the total energy scattered on to the large sphere is equal to the total energy striking the drop. Thus we reach a new expression for  $\psi$ , more suited to calculation

$$\psi = \frac{\left\{ \begin{array}{c} \text{energy per second scattered on to unit area normal} \\ \text{to ray at a distance } r \end{array} \right\} \times 4\pi r^2}{(\text{total energy per second on drop})} \quad (25)$$

The distribution of  $\psi$  is shown in figs. (2) and (3). The polar diagram, fig. (2), represents a solid of revolution rather like a prolate spheroid with

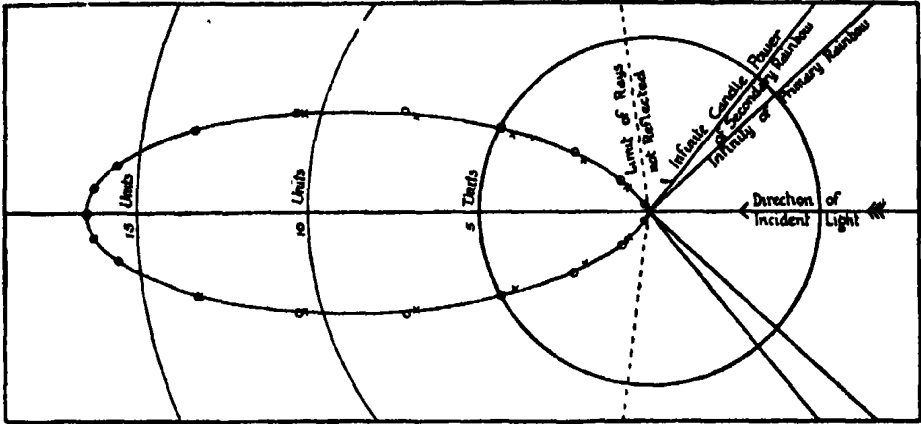


FIG. 2.—Polar Diagram of Candle-power of a Sphere of Water Illuminated by Parallel Light. Refractive index 1.332. Diffraction neglected.

The unit is the mean-spherical-candle power. The line represents the distribution for unpolarized light; the crosses for light polarized so that the magnetic vector is in the plane of incidence, the circles when the electric vector is in the plane of incidence.

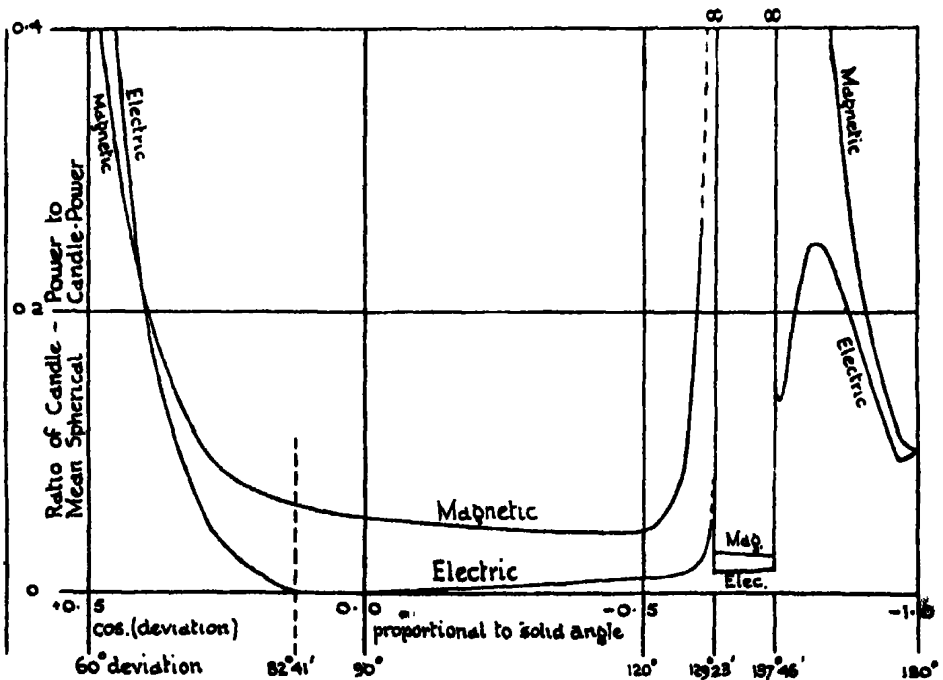


FIG. 3.—Candle Power of a Sphere of Water Exposed to Parallel Incident Light : Detail for Deviations 60° to 180°.

The polarization is indicated by stating the vector, magnetic or electric, which lies in the plane of incidence. Refractive index 1.332. Diffraction is neglected.

two conical shells attached to one end. It shows that the scattered light does indeed mainly go forward or backward rather than sideways, thus so far justifying the division of directions into two hemispheres. The backwardly directed light, which is too small to show on this scale, except at the infinities, is exhibited in fig. (3), in which the abscissa is proportional to area on the sphere at infinity.

If there were a uniform stratus cloud so thin that its droplets did not hide behind each other, then its brightness ought to be proportional to  $\psi$ , multiplied by the secant of the zenith distance of the portion of cloud observed. In this connection it is interesting to note that the polarisation at  $90^\circ$  from the sun, for a single drop, is such that  $\psi = 0.0543$  when the magnetic vector lies in the plane containing the sun, the cloud, and the observer; and by  $\psi = 0.0028$  when the electric vector is in this plane. Here  $\psi$  is proportional to the intensity of the light, and there is of course no relation between the phases of these polarisations, so that the light is not quite plane-polarised.

Now, as to the method by which these diagrams and numbers have been computed. A ray of light striking a sphere of water at an angle of incidence,  $\alpha$ , is divided into two, one part reflected, the other entering the drop at an angle of refraction here called  $\beta$ .

The entering ray is further subdivided by repeated impacts on the surface, at each of which the angle between the ray and the normal to the surface is the same, being  $\alpha$  for the external ray,  $\beta$  for the internal. Now it is known\* that if incident light is polarised in the plane of incidence it remains so after reflection or refraction by water. The same is true for light polarised at right angles to the plane of incidence, but not for polarisations in intermediate planes. The reflectivity depends upon the polarisation, being, according to Fresnel's formulæ

$$\left[ \frac{\sin(\alpha - \beta)}{\sin(\alpha + \beta)} \right]^2 \quad \text{or} \quad \left[ \frac{\tan(\alpha - \beta)}{\tan(\alpha + \beta)} \right]^2 \quad (25, 26)$$

respectively, according as the magnetic or the electric vector is in the plane of incidence. If then either of these vectors lie in the diametral plane of the sphere at the point where the ray first strikes it, the reflectivity will remain the same at each successive impact, and the polarisation of the emergent portions of the ray will have the same relation to the diametral plane in which the ray lies. For this reason these two polarisations must be computed separately. The desired result for unpolarised light is obtained at the end of the process by taking the mean.

To simplify the treatment of the infinities which represent the rainbows, it

\* Drude's 'Optics,' Chap. II.

is convenient to imagine the sun replaced by an ideal star, infinitely small and bright.

The angle of incidence,  $\alpha$ , may be used as a measure of position on the water-sphere. The portion of the sphere included in  $d\alpha$  catches a fraction,  $\sin 2\alpha \cdot d\alpha$ , of the whole energy which strikes the sphere. This energy is distributed among various rays, deviated from the incident direction through angles  $\gamma$ . The area of the portion lying within  $d\gamma$  of a very large sphere of radius  $r$  is  $2\pi r^2 \sin \gamma \cdot d\gamma$ . Thus, if all the light falling on  $d\alpha$  went to this single portion  $d\gamma$ , then  $\psi$  would be equal to

$$\frac{2 \sin 2\alpha \cdot d\alpha}{\sin \gamma \cdot d\gamma}. \quad (27)$$

Actually  $\psi$  is the sum of a number of such terms, one for every fraction of the ray, and each multiplied by  $\sigma$  for every reflection, and by  $(1-\sigma)$  for every refraction which this portion of the ray has undergone, where  $\sigma$  is the reflectivity corresponding to  $\alpha$  and to the polarisation.

The deviations,  $\gamma$ , of the successive fractions are easily shown to be

Once reflected .....	$\gamma_1 = 2\alpha - \pi,$	}	(28)
Refracted, refracted .....	$\gamma_2 = 2(\alpha - \beta).$		
Refracted, reflected, refracted .....	$\gamma_3 = 2(\alpha - \beta) + \pi - 2\beta,$		
Refracted, twice reflected, refracted ...	$\gamma_4 = 2(\alpha - \beta) + 2(\pi - 2\beta).$		

The light more than twice internally reflected has been neglected. This is justifiable, because its intensity would be multiplied by  $\sigma^3(1-\sigma)^2$ , or by smaller quantities, none of which become appreciable except over a zone which catches very little incident light.

Now, when we attempt to count up areas under the curves in fig. 3, in order to find the radiation going backwards, we are baffled by the presence of the infinities. But the difficulty about infinite candle-powers may be entirely avoided by replacing integrations over the sphere-at-infinity by corresponding integrations over the surface of the drop. Thus, the light turned "backwards" is made up of—

(i) Light once reflected at angles of incidence between  $0^\circ$  and  $45^\circ$ . This, expressed as a fraction of the whole light striking the drop, amounts to

$$\int_{\alpha=0}^{\alpha=45^\circ} \sigma \cdot d(\sin \alpha)^2, \quad (29)$$

because  $(\sin \alpha)^2$  is proportional to the whole amount of light striking the drop for angles of incidence between 0 and  $\alpha$ . The reflectivity,  $\sigma$ , computed from formulæ (25) and (26), runs as follows, for a refractive index of 1.332 :—

Angle of incidence.	Magnetic vector in plane of incidence.	Electric vector in plane of incidence.
0°	0·0203	0·0203
5°	0·0205	0·0200
10°	0·0212	0·0193
20°	0·0244	0·0166
30°	0·0308	0·0119
40°	0·0429	9·0058
45°	0·0528	0·0028
50°	0·0665	0·0005
53° 6' 2"	0·0779	0·0000
60°	0·1147	0·0043
70°	0·2191	0·0473
80°	0·4564	0·2888
85°	0·6733	0·4822
90°	1·0000	1·0000

On plotting these as a function of  $(\sin \alpha)^2$ , or what is equivalent and more convenient, as a function of  $\cos 2\alpha$ , since  $d(\sin \alpha)^2 = -\frac{1}{2}d(\cos 2\alpha)$ , it is found that the integral (29) comes to 0·0111 for the mean of the two polarisations. That is to say, for unpolarised light; for the reflectivity is not the ratio of the vectors after and before reflection, but the ratio of their squares.

(ii) The primary rainbow and other light once reflected inside the drop. All this goes "backwards." The intensity is reduced in the ratio  $\sigma$  at the reflection, and in the ratio  $(1-\sigma)$  at each of the two refractions. So this part, as a fraction of the whole light incident on the drop, amounts to

$$\int_{\alpha=0}^{\alpha=90^\circ} \sigma (1-\sigma)^2 d(\sin \alpha)^2. \quad (30)$$

(iii) The secondary rainbow and most of the other light, which is twice reflected inside the drop, but not quite all of it, for one of the equations (28) shows that  $\gamma_4$  is less than  $90^\circ$  when  $\alpha$  lies between  $0^\circ$  and  $39^\circ$ . Accordingly, this backwardly directed part, as a fraction of the whole light incident on the drop, amounts to

$$\int_{\alpha=39^\circ}^{\alpha=90^\circ} \sigma^2 (1-\sigma)^2 d(\sin \alpha)^2. \quad (31)$$

(iv) The tertiary rainbow is directed forward. The higher rainbows are negligible.

Now adding integrals (30) and (31), we get

$$\int_{\alpha=0}^{\alpha=90^\circ} \sigma (1+\sigma) (1-\sigma)^2 d(\sin \alpha)^2 - \int_{\alpha=0}^{\alpha=39^\circ} \sigma^2 (1-\sigma)^2 d(\sin \alpha)^2. \quad (32)$$

The first integral in (32) has been evaluated as an area on a diagram for the two polarisations separately; with the result that the mean for

unpolarised light is 0.0491. The second integral in (32) appears as a small correction, which reduces the total from 0.0491 to 0.0488.

Adding to 0.0488 the integral (29) in amount 0.0111, it follows that a fraction

$$0.0599$$

of the sunlight striking the drop is scattered into the hemisphere which we call the backward direction.

We are now in a position to evaluate  $\int Cdh$ , which is required for equation (28). Here  $C$  is the fraction of the radiation turned backward by the scattering in unit length of ray. But the whole radiation incident upon drops in a length  $dl$  of ray is equal to the intensity of radiation multiplied by  $Andl$ , where  $A$  is the area of the diametral plane of a drop, and  $n$  the number of drops per volume. Therefore

$$C = 0.0599 An.$$

Then  $\int Cdh$  taken across a cloud =  $0.0599 \int Andh$ , which, as before, is equal to

$$\frac{1}{2} \times 0.0599 \times \frac{(\text{volume of liquid per horizontal area of cloud})}{(\text{diameter of particle})}, \quad (33)$$

and from (23) this is equal to

$$\left\{ \frac{S \cos \zeta}{\sqrt{2 E_s}} - 1 \right\} \frac{1}{1-B}, \quad (34)$$

which gives us what we require.

For instance, for a strato-nimbus from which rain fell on the afternoon of 24 May, 1918, I found by photometer measurements with red light of wave-length 0.6 to 0.8 microns, that  $S \cos \zeta / E_s$  was equal to 4.0, the sun's elevation being such that  $\cos \zeta$  was 0.75. The reflectivity of the grass land was of the order of 0.15. Inserting these numbers in the formulæ, we find that the *volume of liquid per horizontal cm.<sup>2</sup> of cloud amounted to 24 diameters of the cloud-droplets.*

This figure is greater, as it should be, than the largest number of diameters, namely, four, determined by the "contrast" method for a stratus which just allowed the sun's disk to be seen.

Possible developments are the improvement of the above treatment by taking a less crude, but still finite, division of directions in space; or else by proceeding to infinite subdivision by means of Fredholm's integral equation,\* having a kernel involving the function  $\psi$ , which is shown in figs. 2 and 3. A method for measuring the diameter of the cloud-droplets is also needed.

\* 'Cambridge Tracts in Mathematics,' No. 10, by Maxime Bôcher.

*Magnetic Storms of March 7-8 and August 15-16, 1918, and  
their Discussion.*

By C. CHREE, Sc.D., LL.D., F.R.S.

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§1. A recent paper\* described the records obtained at Kew and Eskdalemuir Observatories of a world-wide magnetic storm which occurred on December 16-17, 1917. The outstanding feature was the much larger size of the disturbance at the more northern station. This seems a general fact, of which the two magnetic storms discussed in the present paper afford further evidence. They were two of the principal storms of 1918. Their joint discussion affords an opportunity of emphasising the variety in the phenomena exhibited by storms of the same class. The results differ so much from some which Dr. S. Chapman† has given in a recent paper as representative of world-wide magnetic storms, that it may not be amiss to explain that the two storms were selected before the appearance of Dr. Chapman's paper. The storm of March 7-8 was suggested by the kindness of the Director of the Meteorological Service of Canada in sending me, unasked, copies of the D (declination), H (horizontal force), and V (vertical force) curves from Agincourt (near Toronto). Eskdalemuir curves for that date and also for the second storm, which occurred on August 15-16, were kindly supplied by Dr. Crichton Mitchell. The Eskdalemuir magnetographs record N (north component) and W (west component), instead of H and D as at Kew and Agincourt. The simplest way to a comparison was to calculate H and D changes at Eskdalemuir from the observed N and W changes.

The two storms are undoubtedly of the kind discussed by Dr. Chapman, according to whom‡ "apparently all great world-wide magnetic storms commence simultaneously to within a few seconds, over the whole earth, although small local fluctuations may sometimes mask the commencement at particular stations." All I think we can really say is that the particular form of disturbance known as a "sudden commencement," or Sc, which precedes a considerable number of world-wide storms, appears simultaneously at all stations, to the degree of accuracy with which time can be measured on ordinary curves. This conclusion has been reached independently by several recent investigators, including Dr. Chapman and myself.§ Accuracy to

\* 'Roy. Soc. Proc.,' A, vol. 94, p. 525.

† 'Roy. Soc. Proc.,' A, vol. 95, p. 61.

‡ *Loc. cit.*, p. 62.

§ 'Proc. Phys. Soc.,' London, vol. 23, p. 49; vol. 26, p. 137.

half-a-minute in time measurements is a high claim, and the instant at which a movement becomes visible is not wholly independent of the sensitiveness of the instrument. If Dr. Chapman is correct in stating that all world-wide storms commence simultaneously, we must I think suppose that all have Sc's. If so, these must be "masked" more often than not. The existence of an Sc is important in relation to the question whether storms recur after a definite interval. When Mr. W. Maunder\* claimed to have established a 27·3-day recurrence period, this aspect of the case was dealt with in a review of his paper which I contributed to "Terrestrial Magnetism."† Of the 276 storms in Mr. Maunder's list for the period 1882 to 1903 only 77, or 28 per cent., were credited by him with an Sc. In many cases of world-wide storms disturbance seems to originate gradually. The storm of December 16-17, 1917, is a case in point. On that occasion the growth of disturbance was so rapid that I concluded "its commencement may be accepted without hesitation as occurring between 8 h. and 9 h." Often, however, differences of several hours occur in the estimate of the time of commencement made at different stations. Also, an Sc is only sometimes immediately followed by large disturbance. Often a comparatively quiet time intervenes between the Sc—which possesses at most stations a characteristic form—and the large movements, which in the absence of an Sc would be recognised as a storm. In some cases there is room for doubt whether there is a real connection between the Sc and the subsequent storm. There is all the more reason for hesitation on this point because, in a considerable number of cases, the Sc itself is the principal movement. It is followed in some instances by what I have described as a "crest." In low or mean latitudes the Sc is mainly an H movement and is seldom visibly oscillatory, H undergoing a considerable rise in the course of a few minutes. The "crest" consists essentially in the maintenance of the enhanced value of H, the curve presenting a nearly level ridge for a considerable time, which may amount to several hours. A rapid fall, somewhat like an inversion of the original Sc, then ensues, and there may be no further disturbance worth mentioning.

If an Sc were always the immediate precursor of large movements, and if these took an invariable or nearly invariable course, similar stages in the development being reached after definite intervals, there would be much to be said for Dr. Chapman's "storm time," or time measured from the beginning of the storm. If, however, as I suspect to be nearer the truth, the sequence of events is by no means uniform, even in storms having Sc's, the deduction after Dr. Chapman's method of mean results derived from a number of storms

\* 'Monthly Notices, R. A. S.,' vol. 65, p. 2.

† 'Terrestrial Magnetism and Atmospheric Electricity,' vol. 10, p. 9.



superposed according to "storm-time," may give origin to data of uncertain physical significance. It may be a case of combining essentially heterogeneous material.

In connection with the discussion of the magnetic results of the Antarctic Expedition of 1911-12, I have studied the records of many magnetic storms at eight or ten stations, and, during the last 20 years, records of many storms at Kew, Falmouth, and Eskdalemuir have come under my notice. There are certain features which tend to be common, including the well-known depression in  $H$ , most usually experienced sooner or later in large storms, and the modification and great enhancement of the diurnal variation in  $V$ —first described, I believe, in the case of Kew Observatory—but the phenomena, while markedly influenced by local time, have been very variable as regards "storm time."

§ 2. The two storms now to be discussed, unlike that of December 16-17, 1917, have prominent  $Sc$ 's; also large disturbance immediately followed. I have preferred, however, to refer them to ordinary G.M.T. hours, principally for reasons already stated, but partly for the practical reason that the time-breaks in the curves favour that course.

The curves of December 16-17, 1917, were measured at 4-minute intervals, mainly with a view to a special enquiry into Bidlingmaier's "Magnetic Activity." The labour involved in 4-minute measurements is great, and when there are large short-period oscillations, as in the two storms of 1918, individual measurements are apt to be uncertain, as a difference in the setting of the scale equivalent to 1 minute of time may answer to a large difference of ordinate. Accordingly, on the present occasion I have estimated mean hourly values, using a scale in the way originally introduced at Potsdam. This method has been used when measuring electric potential curves at Kew for a number of years, with satisfactory results. In careful hands it gives wonderfully consistent results, even with highly oscillatory curves.

The mean hourly values during the two storms are given in Tables I and II as differences from certain standard values. Details as to the ranges during the  $Sc$ 's and the whole disturbance, and as to instantaneous and mean values for certain specified times, are given in Tables III and IV. All declination data are given in terms of the equivalent force. The difficulty of settling standard or normal values was discussed in my previous paper. As my information for Agincourt and Eskdalemuir was confined to the curves received, and uniformity of procedure was desirable, I have accepted as the normal value in each case the mean from 2 h., 8 h., 14 h., and 20 h. L.M.T. during the 24 hours preceding the storm. The mean from these

Table I.—Mean Hourly Values. March 7-8, 1918.

Hour, G.M.T.	Eskdalemuir.					Kew.			Agincourt.		
	N.	W.	H.	D.	V.	H.	D.	V.	H.	D.	V.
	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.
20.5	- 4	- 5	- 5	- 4	+ 3	+ 3	+ 2	+ 5	+ 6	+ 16	0
21.5	+ 23	+ 1	+ 22	- 6	0	+ 28	0	+ 5	+ 35	+ 15	+ 1
22.5	+ 5	- 16	0	- 17	- 4	+ 12	- 9	0	+ 38	+ 10	+ 2
23.5	- 22	- 51	- 36	- 42	+ 10	- 25	- 31	+ 3	+ 12	+ 21	+ 5
0.5	- 80	- 101	- 106	- 73	- 62	- 49	- 58	- 14	+ 75	+ 46	+ 67
1.5	- 149	- 187	- 197	- 135	- 205	- 35	- 107	- 74	+ 95	+ 4	- 100
2.5	- 263	- 259	- 327	- 170	- 205	- 136	- 175	- 142	+ 205	+ 39	- 179
3.5	- 164	- 165	- 205	- 110	- 134	- 148	- 101	- 94	- 107	- 20	- 130
4.5	- 159	- 16	- 157	+ 31	- 98	- 112	+ 32	- 43	- 217	- 58	- 121
5.5	- 52	- 32	- 59	- 15	- 39	- 80	- 12	- 18	- 37	- 27	+ 21
6.5	- 57	- 35	- 65	- 17	- 6	- 77	- 9	- 3	- 83	+ 13	+ 17
7.5	- 67	- 40	- 76	- 18	+ 5	- 77	- 11	+ 3	- 181	+ 75	- 28
8.5	- 75	- 35	- 82	- 11	+ 9	- 80	- 6	+ 8	- 90	+ 18	- 6
9.5	- 77	- 32	- 83	- 8	+ 11	- 83	- 3	+ 18	- 61	- 6	+ 7
10.5	- 79	- 27	- 83	- 3	+ 15	- 83	+ 9	+ 19	- 63	+ 6	+ 14
11.5	- 85	- 19	- 87	+ 7	+ 21	- 94	+ 14	+ 21	- 56	- 1	+ 17
12.5	- 76	- 14	- 77	+ 9	+ 24	- 88	+ 16	+ 26	- 53	- 9	+ 20
13.5	- 71	- 13	- 72	+ 9	+ 27	- 83	+ 17	+ 29	- 55	- 13	+ 20

Table II.—Mean Hourly Values. August 15-16, 1918.

Hour, G.M.T.	Eskdalemuir					Kew.		
	N.	W.	H.	D.	V.	H.	D.	V.
	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.
14.5	- 20	+ 29	- 11	+ 34	- 7	- 10	+ 39	- 2
15.5	+ 10	+ 18	+ 15	+ 14	- 7	+ 18	+ 49	+ 5
16.5	+ 28	+ 68	+ 47	+ 57	- 10	+ 47	+ 55	- 3
17.5	+ 97	+ 72	+ 114	+ 40	0	+ 87	+ 37	+ 22
18.5	+ 184	+ 122	+ 212	+ 62	+ 22	+ 152	+ 40	+ 70
19.5	+ 90	+ 40	+ 98	+ 12	+ 83	+ 47	- 3	+ 80
20.5	+ 140	+ 55	+ 150	+ 11	+ 136	+ 25	- 2	+ 102
21.5	- 9	- 5	- 10	- 2	+ 36	- 9	- 9	+ 51
22.5	- 60	- 66	- 77	- 45	- 48	- 37	- 40	+ 14
23.5	+ 5	- 39	- 7	- 39	- 12	- 21	- 36	+ 11
0.5	- 3	- 42	- 15	- 39	+ 11	- 26	- 33	+ 13
1.5	- 10	- 28	- 18	- 24	+ 17	- 29	- 18	+ 13
2.5	- 62	- 9	- 62	+ 10	- 6	- 40	+ 10	+ 10
3.5	- 83	- 16	- 84	+ 9	- 81	- 42	+ 12	- 2
4.5	- 56	- 19	- 59	- 2	- 57	- 45	+ 1	- 10
5.5	- 21	- 10	- 23	- 3	- 33	- 22	- 7	- 2
6.5	- 15	- 29	- 23	- 23	- 8	- 22	- 17	+ 6
7.5	- 13	- 29	- 21	- 24	+ 7	- 21	- 22	+ 14

four hours in the average day comes very near the mean for the day in all the magnetic elements. Greenwich time was accepted as local time for Kew (51° 28' N.; 0° 19' W.) and Eskdalemuir (55° 19' N.; 3° 12' W.), and time



of  $75^{\circ}$  W. as local time for Agincourt ( $43^{\circ} 47'$  N.;  $79^{\circ} 16'$  W.). This procedure was less satisfactory for the August than the March storm, because August 14 was slightly disturbed, and the afternoon V-trace at Eskdalemuir was more affected than is usual with so comparatively trifling a disturbance. The Sc on March 7 began about 21 h. 10 m. G.M.T., and that on August 15 about 15 h. 50 m. The first hours included in Tables I and II entirely precede the storm, and anyone who prefers the values from these hours as standards can easily make the necessary changes in the Tables. The mean value of H for the hour commencing at the Sc will be found in Table IV by anyone desiring a more exact comparison with Dr. Chapman's results.

An unfortunate feature on both occasions was loss of trace at Eskdalemuir. There was also loss of H-trace at Agincourt, where the oscillations were so large that the trace went off the sheet on both sides. The absence of the trace from the Agincourt sheet was short, except between 2 h. 10 m. and 3 h. 10 m. G.M.T. on the plus side, and between 3 h. 30 m. and 4 h. 15 m. on the minus side; but during these intervals the marginal values—which had to be accepted as the true values—may have been considerably exceeded. This is indicated by the + sign attached to the entry under 2.5 h., and by the — sign attached to the entries under 3.5 h. and 4.5 h. in Table I. The values for the adjacent hours are slightly affected, but are probably nearly correct. At Eskdalemuir, on August 15, the V-trace was off the sheet on the plus side between 20 h. and 21 h., but only for a short time, and the excess over the marginal value was probably small; still, the entry in Table II is an underestimate. On March 7-8 the loss at Eskdalemuir was more serious. It happened to be the second day's trace, so the curves naturally started below the middle of the sheet, and all three elements had, unfortunately, an exceptionally large fall. The N- and W-traces were off the sheet on the minus side several times, and for over an hour continuously in either case. The V-trace was off only once, but then for two hours. Thus, in accepting the marginal value, a very considerable underestimate was probably made of the depression, and so of the range of force during the storm. The hourly values in Table I, to which the minus sign is attached, ought probably to be very considerably lower.

A general idea of the sequence of events is most easily derived from fig. 1. There is a sensible resemblance between the H-curves for March 7-8 at Kew and Eskdalemuir and the H-curves in Chapman's fig. 1. There is the characteristic rise in H for the first hour or half-hour of the storm, and then a marked fall. But whereas the rise in the mean value for the first hour is not so very much larger than Chapman's, the subsequent fall is enormously

greater, and takes place in shorter time. Chapman,\* it is true, remarks on an "increasing lateness of the epoch of minimum horizontal force, with

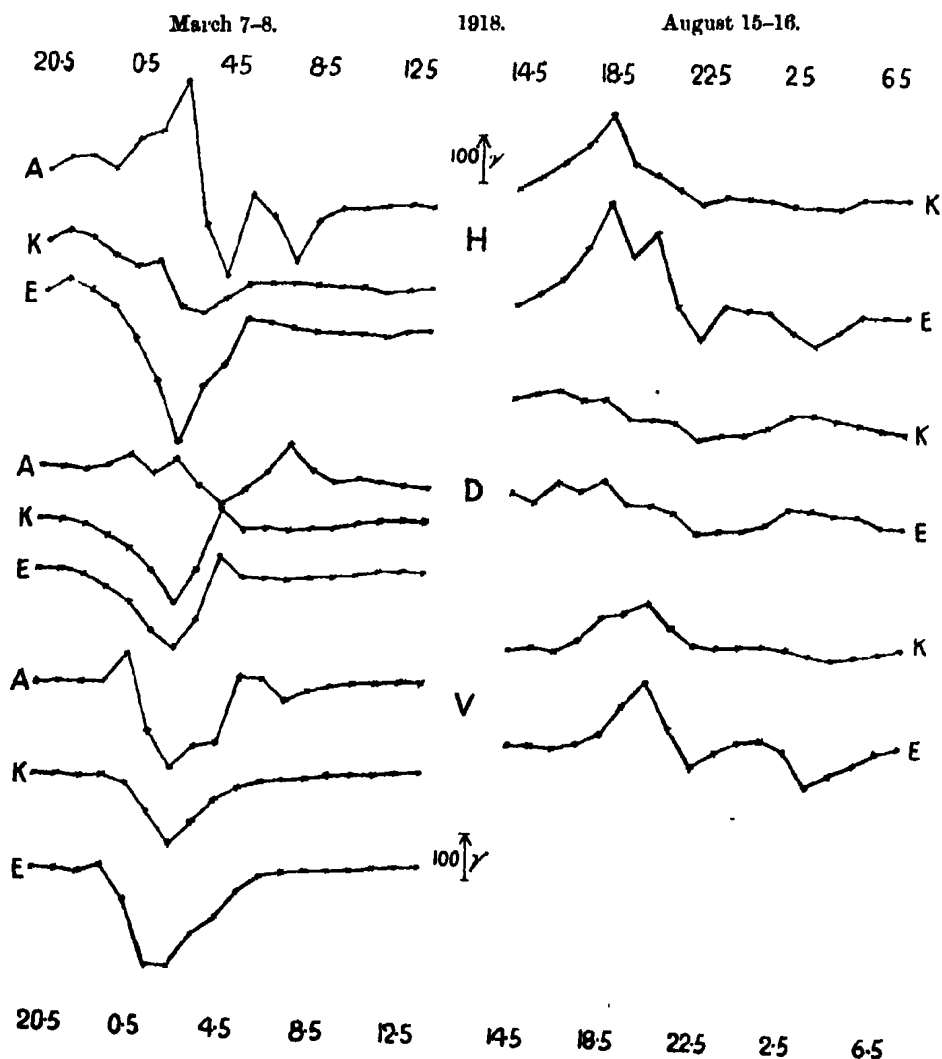


FIG. 1.—Times are G.M.T.

A = Agincourt.

K = Kew.

E = Eakdalemuir

H = Horizontal Force.

D = Declination.

V = Vertical Force

diminishing storm intensity," which implies an acceleration when disturbance is large.

The question as to whether mere size affects the phase of magnetic storms

\* *Loc. cit.*, p. 72.

arose incidentally in the discussion of Mr. Maunder's results already referred to. He had divided storms into four classes according to size. Taking his classes in descending order of magnitude, and accepting his figures, I found the respective average durations to be 29.1 h., 34.4 h., 33.9 h., and 26.2 h., and concluded, "if we exclude the very largest disturbances, whose number is very limited (16 out of 276), we have apparently a distinct tendency for the duration to be least in the weaker storms." This is not necessarily incompatible with Chapman's conclusions, but it is decidedly against any marked acceleration of phase with increase of intensity. Unless Chapman himself had supposed the acceleration to be small, he would hardly have derived his results, as one infers he did, from the superposition of storms irrespective of their size.

While the Kew and Eskdalemuir H diagrams for March 7-8 have a resemblance to Chapman's fig. 1, it is otherwise with the Agincourt H diagram for the first part of the storm. We have, of course, the usual rise during the Sc, but, instead of falling, the general trend in H is upwards. The mean value for the sixth hour "storm-time" exceeded that for the first hour storm-time by at least 170  $\gamma$ . The maximum at Agincourt occurred practically simultaneously with the minimum at Kew and Eskdalemuir.

Chapman seems to regard the pole of the zonal harmonic of the first order in the Gaussian potential as decisive in the phenomena of magnetic storms. It is obviously fundamental in the Birkeland-Störmer theory, because the paths of the electrical ions or corpuscles coming from the sun are determined by the earth's magnetic field, and at distances from the earth large compared with the earth's radius, the first order terms in the potential will naturally predominate. But when we come to the actual distribution of electrical currents in aurora, at heights of the order of 100 kilom., there is no such obvious reason for the supposed preponderance of the first order terms. Be this as it may, the interesting point at the moment is that, if we accept Chapman's position ( $80^{\circ}$  N.,  $70^{\circ}$  W.) for the magnetic pole (from the zonal harmonic), we find for the magnetic latitudes of Agincourt, Kew, and Eskdalemuir the respective values  $53.6^{\circ}$ ,  $53.9^{\circ}$ , and  $57.9^{\circ}$ . Thus Agincourt and Kew have practically the same magnetic latitude. Consequently, in accordance with Chapman's views, we should naturally expect the disturbance phenomena at the two places to be similar. There is, of course, five hours' difference in the local time, and it may be suggested that the difference in the H variations represents Chapman's "local storm variation," by which he means apparently the difference between the diurnal variations characteristic of disturbed and ordinary

days. I have shown, however, in the case of Kew\*—and other European stations agree—that the type of the diurnal variation in  $H$  on disturbed days makes no very great departure from that for ordinary days, and the changes during the six hours commencing at 21 h. are small. Thus the true explanation of the difference remains to be found.

§ 3. Dr. Chapman's statement† as to the later phenomena in  $H$ —"A period of recovery then follows, and lasts for several days. Both the decrease and the recovery proceed most rapidly after their initial stages, and gradually slow down"—is I think a fair statement of the average facts; but the recovery is not very marked in fig. 1, and is irregular, as is usual in individual cases. His further statement‡ "This recovery shows itself in the non-cyclic variation on quiet days" is I think premature. This explanation of the large n.c. rise in  $H$  on quiet days naturally suggests itself, and was in fact pointed out in my first paper§ describing the phenomenon. But in a subsequent paper|| I mentioned a second possibility, which so far as I know has not yet been disproved. The phenomena are rather suggestive of what happens with a permanent magnet, especially if of steel of poor retentiveness and recently magnetised, when subjected to a magnetic, mechanical, or thermal shock. There is an immediate loss of magnetic moment, with a tendency to recovery during a subsequent rest. The loss is determined partly by the magnitude of the shock, partly by the recent history of the magnet. The rise of moment during the rest may be a consequence of the fall occasioned by the shock. On the other hand, the fall consequent on the shock may arise from the moment of the magnet having been previously raised above a reasonably stable position. It is conceivable that, owing to the earth's rotation, or some other property, the horizontal intensity has a tendency to rise above what is altogether stable, a tendency which manifests itself in the n.c. change in quiet days, and that the decrease characteristic of magnetic storms is a shock effect, really the consequence of this.¶ The two explanations are not necessarily exclusive; each may be partly true. At present I can only say that conclusive evidence one way or another is not so easily got as might be supposed *a priori*. The two storms under consideration are well adapted to illustrate the difficulties. The observed n.c.  $H$  changes on all the early days in March to which "character" 0 was allotted at Kew were as follows:

\* 'Phil. Trans.,' A, vol. 210, pp. 283, 286 and 290.

† *Loc. cit.*, p. 62.

‡ *Loc. cit.*, p. 66.

§ 'British Association Report for 1895,' p. 209 (specially p. 212).

|| 'British Association Report for 1896,' p. 231 (specially p. 237).

¶ Since this was written I have found a very similar suggestion in § 129 of Balfour Stewart's article on Terrestrial Magnetism in the 'Encyclopædia Britannica,' 9th edition.

+7  $\gamma$  on 5th, -2  $\gamma$  on 6th, +13  $\gamma$  on 9th, -5  $\gamma$  on 13th, and +5  $\gamma$  on 14th. We thus get +2.5  $\gamma$  as the mean from the two quiet days preceding the storm, and +4.3  $\gamma$  as the mean from the three days which followed it. During the 10th, 11th, and 12th, all days of "character" 1, there was a total n.c. rise of +29  $\gamma$ . The 15th and 16th were days of "character" 2. The depression, about 44  $\gamma$ , existing at 24 h. on March 8 was thus practically accounted for before the next large disturbance began, but the greater part of the apparent recovery took place on days of "character" 1.

On August 16 we have regarded the storm as practically ended by 8 h., because that is what is naturally suggested by the appearance of the curves between 5 h. and 8 h. But shortly after 8 h. a very rapid fall took place in H at Kew and in N at Eskdalemuir. By 10 h. H at Kew had fallen to 153  $\gamma$  below what we have accepted as standard value. If we regarded this as part of the storm which commenced on the 15th, it would raise the H range at Kew from 338  $\gamma$  to 436  $\gamma$ , and diminish the lowest mean hourly value from -49  $\gamma$  to -132  $\gamma$ . But this fall in H was followed by so large and rapid a rise that practically no depression remained by the end of the day. There was a very quiet time on both the 15th and 17th from 1 h. to 5 h., and if we derive mean values of H from these four hours we find the value on the 15th only 4.5  $\gamma$  in excess of that on the 17th. There immediately followed—a very unusual feature after large storms—seven consecutive days to which "character" 0 was awarded at Kew. The successive n.c. changes were +11  $\gamma$ , +9  $\gamma$ , +8  $\gamma$ , -9  $\gamma$ , +8  $\gamma$ , -3  $\gamma$ , and +8  $\gamma$ . This represents a net rise of 32  $\gamma$ , or 27  $\gamma$  in excess of the apparent depression remaining on the morning of the 17th. The mean of the n.c. changes from these seven days is about the average for quiet days. In calculating these n.c. changes mean ordinates from 60 minutes centering at the hour were accepted for the respective midnights, and it was assumed that there was no real change in the base value of the curves after making due allowance for the temperature changes in the magnetograph room. In view of facts such as the above, one can only recommend caution in accepting as final any conclusions as to the cause of the dominant n.c. change in H on quiet days.

§4. Reverting to fig. 1, the very close resemblance between the D changes at Kew and Eskdalemuir should be noticed. As Table III shows, D had a very much bigger range at Agincourt on March 7-8 than at Kew or Eskdalemuir, but the oscillations at Agincourt were much more nearly about a mean value, and if we had before us only mean hourly values we should greatly underestimate the disturbance. It is noteworthy that the extreme easterly position at Agincourt in fig. 1 synchronises with the extreme westerly position at Kew and Eskdalemuir.



On March 7-8 the V curves at Kew and Eskdalemuir show the depression characteristic of the early morning hours during magnetic storms, while on August 15-16 they show the elevation characteristic of the afternoon. It appears, however, decidedly later in the day than usual.\* On March 7 the afternoon elevation is practically absent at Kew and Eskdalemuir—possibly on account of the late hour when the storm began—and is but poorly represented at Agincourt, though the storm began there near 16 h. L.M.T. A somewhat unusual feature—represented, however, in the storm of December 16-17, 1917—is the double bay in the Eskdalemuir V-trace in the night of August 15-16.

Mean hourly values by themselves may give an inadequate idea of the activity of the disturbance. Table I, for instance, might almost suggest that on March 7-8 declination was less disturbed at Agincourt than Kew. The figures for the hourly ranges in Tables V and VI will help to a truer conception of the facts. During the most active part of the storm, from 0 h. to 5 h. G.M.T. on March 8, the hourly ranges were enormously greater at Agincourt than Kew. H at Kew is 15 per cent. higher than at Agincourt, so the excess in the angular movements at Agincourt was even

Table V.—Hourly Ranges. March 7-8, 1918.

Hour, G.M.T.	Eskdalemuir.			Kew.			Agincourt.		
	N.	W.	V.	H.	D.	V.	H.	D.	V.
20-21	7.	7.	7.	7.	7.	7.	7.	7.	7.
21-22	10	9	1	6	5	—	10	6	1
22-23	82	28	7	59	24	—	110	59	13
23-24	73	95	15	77	50	—	53	48	12
0-1	29	35	19	90	24	—	43	29	11
1-2	150	91	117	76	46	32	163 +	134	110
2-3	194 +	197 +	84 +	97	163	96	360 +	582	507
3-4	174 +	80 +	—	194	102	45	244 +	270	125
4-5	196 +	165 +	130 +	71	220	88	672 +	529	310
5-6	241	152	67	107	88	—	494 +	154	304
6-7	98	77	54	35	40	—	115	65	36
7-8	65	50	21	35	32	—	91	48	27
8-9	70	45	6	32	32	—	101	92	57
9-10	45	40	6	24	35	—	84	48	36
10-11	40	40	6	30	35	—	43	36	14
11-12	116	112	13	65	54	—	108	59	37
12-13	41	32	8	21	16	—	48	33	17
13-14	25	17	5	18	8	—	22	24	7
14-15	18	12	3	15	11	—	24	12	7

\* The usual hour of the maximum in V on disturbed days at Kew Observatory is from 17 h. to 18 h. See 'Phil. Trans., A, vol. 210, pp. 264-286.

Table VI.—Hourly Ranges. August 15-16, 1918.

Hour, G.M.T.	Eskdalemuir.			Kew	
	N.	W	V	H.	D
14-15	7	7.	7	7.	7.
15-16	15	10	5	18	10
16-17	181	134	14	136	64
17-18	70	38	11	41	19
18-19	263	153	30	183	67
19-20	316	161	42	221	40
20-21	92	67	64	40	51
21-22	385	291	131 +	88	113
22-23	89	70	89	52	72
23-24	99	67	81	28	56
0-1	30	16	59	12	16
1-2	40	24	4	19	27
2-3	24	18	8	19	13
3-4	80	43	93	31	44
4-5	32	23	14	31	21
5-6	30	16	32	17	11
6-7	31	27	21	18	16
7-8	20	12	25	18	11
	25	38	8	15	29

greater than Table V suggests. The total range there was approximately  $2^{\circ} 5'$ , and the lowest instantaneous value was nearly  $80'$  below what we have accepted as standard. The deduction of maximum and minimum hourly values for H and D from N and W curves is hardly practicable, so N and W data had to be given for Eskdalemuir in Tables V and VI. Owing to the loss of trace already mentioned, some of the ranges in the Tables are underestimates, and no value at all could be assigned for V at Eskdalemuir between 2 h. and 3 h. on March 8, because the trace was off the sheet all the time. At Kew the artificial disturbance in V forbids the deduction of hourly ranges unless the natural disturbance is large. Values for that element are thus confined to the four most disturbed hours of March 8. They are mainly intended to show the comparative insignificance of the disturbance at Kew.

§ 5. Measurements were made of some of the most rapid rates of change with the following results:—

March 7-8—

Eskdalemuir.....	N	+57 (1), +16 (5), -57 (2), $\pm 21$ (14), $\mp 41$ (6), $\mp 23$ (7);
" .....	W	+27 (1), -23 (5), $\mp 40$ (6), $\mp 16$ (8);
" .....	V	-10 (10), +13 (7);
Kew .....	H	+41 (1), +12 (5), -10 (16), $\mp 19$ (6);
" .....	D	-7 (16), -8 (11), $\mp 17$ (6);
Agincourt.....	H	$\mp 58$ (9), -47 (7½), -89 (7½), +26 (10);
" .....	D	-34 (15), +52 (9), $\mp 115$ (8);
" .....	V	-28 (9), +22 (7), -24 (12), $\pm 23$ (19), $\mp 57$ (8).

August 15-16—

Eskdalemuir.....	N	+184(1), -258(1), +24(11), $\mp 43$ (12), -16(11), +15 (24), -22 (10), +40 (3), -136 (2);
" .....	W	+134 (1), -145 (1), -88 (3), +21 (9);
Kew .....	H	+139(1), -183(1), +14 (11), -9(11), +11 (23), -14 (14);
" .....	D	+56 (1), -67 (1), +12 (9).

The figure outside the bracket gives the rate, the unit being 1  $\gamma$  per minute. The figure inside the bracket gives the duration in minutes of the interval during which the change occurred. The plus sign signifies a numerical rise in H, N, W, and V, or westerly movements in D, the minus sign the reverse. The double sign implies an oscillation, the upper sign applying to the first, the lower to the second movement. For instance,  $\pm 21$  (14) means that the element first increased and then diminished, the times taken to rise and fall together amounting to 14 minutes; 21 represents the result obtained when the numerical sum of the two movements, expressed in terms of 1  $\gamma$  as unit, is divided by 14. Rates from very short intervals, e.g., +57 (1), have a large probable error, as no very exact time measure of so short an interval is possible. The time of an oscillation, especially when the to-and-fro movements are nearly equal, can be measured more accurately than that of a unidirectional movement. In some cases estimates have been given for the separate movements, as well as for the total movement during an oscillation. Most of the estimates were based on measurements made on actual turning points of the curves, but sometimes, where the rate of change fell off markedly near a turning point, the most rapid portion only of the movement was considered. On August 15-16 the very rapid rises of force from 1-minute intervals refer to the rising movement in the Sc, while the very rapid falls

from 1-minute intervals refer to a remarkable movement which occurred nearly 1 h. 40 m. after the Sc.

A remark by Dr. Chapinan\* "The irregular and rapidly changing magnetic variations during a storm are of generally local character" is, I think, true of most very large rapid oscillations. At all events it is usually in such cases that outstanding differences are seen between Kew and Eskdalemuir, or between Antarctic and ordinary latitudes; but it does not apply to Sc movements except in a limited sense. The cause of these movements is operative from pole to pole, and is so effective even near the equator that Prof. Birkeland mistakenly supposed them to be principally developed there. At the same time, the great difference in the amplitude at stations so near together as Kew and Eskdalemuir, and the much greater relative development of the first or falling movement of the oscillation at Eskdalemuir and Agincourt, as compared with Kew, show that the immediate cause must be largely dependent on the geographical position of the station.

§ 6. The principal use made of Tables V and VI was in calculating Bidlingmaier's "Magnetic Activity." This is defined for a particular station as the mean value of  $(1/8\pi)(\alpha^2 + \beta^2 + \gamma^2)$ , where  $\alpha, \beta, \gamma$  denote the departures of the three rectangular components of magnetic force from their standard values. It consists of two parts, called  $A_1$  and  $A_2$  in my previous paper.†  $A_1$  represents what the "activity" would be if during each hour each element remained constantly at its mean value for that hour.  $A_2$  is the contribution to the "activity" from the variations within the hour. In my last paper I calculated  $A_2$  from the formula

$$A_2 = (1/8\pi)(1/n) \sum \eta^2, \quad (1)$$

where the  $n$  values of  $\eta$  represented the departures from the mean value for the hour of the values obtained from measuring the curves at intervals of  $60/n$  minutes. Bidlingmaier's original proposal was to derive  $A_2$  from the hourly range, through certain arbitrary relations based on measurements of the Wilhelmshaven curves. In a discussion‡ of this proposal I pointed out that Bidlingmaier's relations, if accepted, would have the undesired effect of making the calculated value of  $A_2$  depend on the sensitiveness of the magnetograph, and that the only obvious way of avoiding this was to assume

$$(1/n) \sum \eta^2 = CR^2, \quad (2)$$

where  $R$  is the hourly range and  $C$  a constant. From an examination of term-hour curves from a large number of observatories I found that when  $R$

\* 'Monthly Notices, R. A. S.,' vol. 69, p. 74.

† 'Roy. Soc. Proc.,' A, vol. 94, p. 540.

‡ 'Terrestrial Magnetism and Atmospheric Electricity,' vol. 22, p. 57.

was derived from the largest and least hourly ordinates resulting from measurement of the curves at 5-minute intervals, the best value for  $C$  lay between 0.09 and 0.10. In a paper in the same number of 'Terrestrial Magnetism,' Mr. D. L. Hazard\* arrived independently at a very similar result from a study of Cheltenham curves. He proposed 0.10 as the value of  $C$ . I found that the appropriate value for  $C$  fell when the range was derived, not from measurements at regular time intervals, but from the actual maximum and minimum ordinates within the hour. In calculating  $A_2$  from Tables V and VI, I have taken 0.09 as the value of  $C$ ; i.e., I have assumed.

$$A_2 = (1/8\pi)(0.3R)^2. \quad (3)$$

The difficulty of fixing a normal value in calculating  $A_1$  was pointed out in my last paper, where two calculations were made. One set of results, described as  $A_1$ , accepted for the normal the mean value from a quiet period of 24 hours preceding the storm; the other set, described as  $A'_1$ , accepted the mean value for the 24 hours of the storm day itself. The latter choice was impossible in the present case owing to loss of trace. Thus only one set of values was found for  $A_1$ , which accept the normal values already explained in connection with Tables I and II.

In the case of the hourly values in Tables VII and VIII,  $A_1$  and  $A_2$  are not given separately, but only their sum. But the mean values at the foot include separate values for  $A_1$  and  $A_2$  as well as for  $A_1 + A_2$ . These means are in each case derived from the 17 last hours included in the Tables, the hour preceding the storm being left out of account. Apparent inconsistencies of 1 unit in the last place are due to the fact that the calculations were carried to one figure beyond the last retained. The trace being off the sheet from 2 h. to 3 h. on March 8 at Eskdalemuir, 0 had to be assigned as the contribution from  $V$  to  $A_2$ . The other entries to which a + is attached also suffered from loss of trace. Probably  $A_2$  suffered more than  $A_1$  as a rule. At the same time, the percentage of the total "activity" for the horizontal plane at Eskdalemuir due to  $A_2$  in Table VII is practically the same as at Kew, where there was no loss of trace. This percentage is only 9 at these two stations as compared with 37 at Agincourt. In Table VIII the percentage contribution from  $A_2$  is considerably larger at Kew and Eskdalemuir than it was in Table VII, being 28 for the horizontal field at Eskdalemuir and 19 at Kew. The contribution from  $V$  is substantial in both Tables, though much less important relatively than in the storm of December, 1917.

The contribution from  $V$  to  $A_1$  at Kew on August 15-16 is not given in the Table. The mean from the 17 hours was actually 61, bringing up the

\* 'Terrestrial Magnetism and Atmospheric Electricity,' vol. 22, p. 84.



Table VIII.—“Magnetic Activity,” August 15-16, 1918. (Unit  $1 \times 10^{-10}$  erg per cubic centimetre.)

Hour, G.M.T.	Eskdalemuir.					Kew.		
	N.	W.	V.	N + W.	N + W + V.	H.	D.	H + D.
14-15	17	34	2	51	53	5	61	66
15-16	121	77	3	190	201	79	110	190
16-17	49	189	4	238	243	94	122	216
17-18	623	290	0	913	919	422	71	492
18-19	1707	680	26	2393	2418	1096	69	1165
19-20	353	80	290	483	722	94	10	103
20-21	1312	424	798 +	1787	2585 +	53	46	99
21-22	32	19	80	50	130	18	22	35
22-23	179	190	115	368	483	57	96	153
23-24	4	62	18	66	84	18	53	71
0-1	6	72	5	78	83	28	46	74
1-2	6	82	12	88	50	35	13	48
2-3	176	10	32	186	218	67	11	78
3-4	278	12	262	290	552	74	7	81
4-5	128	15	133	144	277	82	1	82
5-6	21	7	45	28	73	20	8	28
6-7	10	34	5	44	49	20	12	32
7-8	9	39	2	48	50	18	22	41
Means								
$A_1 + A_2$	295	132	108	427	535	134	42	176
$A_1$	212	95	97	306	403	108	34	142
$A_2$	83	37	11	120	131	25	8	33

mean value of  $A_1$  from H, D and V combined to 203, or almost exactly half the corresponding result for Eskdalemuir. If we confine ourselves to the horizontal field, but take the complete activity  $A_1 + A_2$ , the Kew mean value was 52 per cent. of the Eskdalemuir value for the March storm, and 41 per cent. of the Eskdalemuir value for the August storm. The former percentage would, however, have been decidedly less but for the loss of trace at Eskdalemuir. These percentages are both less than in the corresponding case for December 16-17, 1917, but the higher is near the percentage obtained on that occasion when the contributions from V were included.

The mean “activity” at Agincourt on March 7-8 is only a little less than that for Eskdalemuir, whether V is included or not; but the Agincourt figures probably suffered less through loss of trace than those for Eskdalemuir. The mean “activity” for the August storm was decidedly less than that for the March storm at both Kew and Eskdalemuir. On these, as on many other occasions, the relative amplitudes of the disturbances were in no way proportional to the amplitudes of their  $Sc$ ’s.

In any comparison with the “activities” calculated for December 16-17, 1917, it is the  $A_1$  not the  $A_1'$  figures that should be taken for the latter. If

we include V the mean "activity" at Eskdalemuir for the 17 hours of March 7-8 was only a shade larger than that for the 24 hours of December 16-17. If we take only the horizontal components the mean "activity" for December 16-17 was very considerably less than that for March 7-8 at both Kew and Eskdalemuir, though still larger than that for August 15-16, 1918. The largest mean hourly "activity" in any of the Tables is that for 2 h. to 3 h. on March 8 at Eskdalemuir. Through an underestimate, owing to loss of trace, it is 44 per cent. larger than the highest value observed on December 16-17, 1917.

Some conclusions can be drawn from the Tables as to the suitability of "magnetic activity," for the purpose for which it was primarily intended, viz., to supply a daily numerical measure of the disturbance at individual stations to replace the magnetic "character" figures 0, 1, 2 in the international scheme on which the selection of quiet days at De Bilt has depended. The chief use of these quiet days is for the calculation of the regular diurnal inequality, and if, as I have suggested, selected disturbed days should also be assigned for that purpose, or if for any reason inequalities should be wanted for several categories of days, it would be particularly important that the criterion employed should discriminate effectively between days having different types of diurnal inequality. Activity of oscillation which did not affect the mean hourly value would obviously be much less fatal to inequalities intended to represent moderately quiet days than would deflections raising or lowering the mean hourly value. On the other hand, if there are large oscillations, the effect on the mean hourly value must inevitably depend sensibly, however the curves are measured, on when the hour happens to fall. Days, in short, when there are large short-period oscillations provide unusual opportunities for the entry of "accidental" features into the diurnal inequality. The fact that  $A_1$  is in general so much larger than  $A_2$  is obviously a point in favour of "magnetic activity." It is also in its favour that on occasions when the oscillations are exceptionally large within the hour, as in the case of D at Agincourt on March 7-8, the contribution from  $A_2$  becomes so large as to be vitally important. While recognising the advantageous features of "magnetic activity," I am doubtful whether they are an adequate offset against the large amount of labour entailed even with the simplified approximate way of calculating  $A_2$  adopted here. I am still inclined to think that the use of absolute daily ranges, in the way which I have suggested elsewhere,\* might as an international scheme give equally satisfactory results in a much simpler way.

§ 7. Some reference is needed to a criticism of "magnetic activity" under

\* 'Terrestrial Magnetism and Atmospheric Electricity,' vol. 22, pp. 80-83.



another name recently made by Dr. Chapman.\* Starting with the Maxwellian energy integral,

$$(1/8\pi) \iiint (\alpha^2 + \beta^2 + \gamma^2) dx dy dz, \quad (4)$$

he shows that if we write  $\alpha_0 + \delta\alpha$  for  $\alpha$ , etc., the integral consists of the following three parts:—

$$(1/8\pi) \iiint \delta\alpha^2 + \delta\beta^2 + \delta\gamma^2 dx dy dz, \quad (5)$$

*i.e.*, the space integral of Bidlingmaier's magnetic activity, which he calls the "self-energy integral";

$$(1/4\pi) \iiint (\alpha_0\delta\alpha + \beta_0\delta\beta + \gamma_0\delta\gamma) dx dy dz, \quad (6)$$

which he calls the "joint-energy integral"; and

$$(1/8\pi) \iiint (\alpha_0^2 + \beta_0^2 + \gamma_0^2) dx dy dz.$$

The last part, as a constant, he leaves out of account. Speaking of the first two parts, he says: "The latter (*i.e.*, the 'joint-energy integral') has usually been neglected on the ground that the permanent and disturbance fields being independent, on the average there will be no net gain or loss due to their superposition." This he holds to be unjustifiable, and concludes that the "joint-energy integral" is "the most important part of the whole excess energy."†

Later,‡ he says, after remarking on Lord Kelvin's estimate of the energy of a magnetic storm, "The other calculations which have been made have usually much underestimated the energy . . . the importance of the joint-energy integral was missed."

As Chapman gives no references, and does not explicitly mention "magnetic activity," I am uncertain whether he had in view the calculations of it made by myself and others, or whether he was referring to some attempts which I have not seen to calculate the energy of a magnetic storm from the "magnetic activity" alone.

"Magnetic activity" has the dimensions of energy, and in my first paper which was devoted to the method of calculating  $A_z$ , the word energy was used freely, but hardly in a way that could lead to misconception. In my paper in the 'Proceedings,' I was careful to use the term "magnetic activity," and pointed out that the Maxwellian integral "is supposed to be taken throughout the whole of the magnetic field. It takes, moreover, as point of departure a total absence of force. In the present case we know the

\* 'Monthly Notices, R. A. S.,' vol. 79, p. 70.

† *Loc. cit.*, p. 73.

‡ *Loc. cit.*, p. 80.

absolute values . . . at a fixed point . . . ; but the intensity of the field never vanishes." In short, I regarded Bidlingmaier's use as really distinct from Maxwell's, the latter's integral having simply suggested the final form adopted by Bidlingmaier, and particularly his use of the factor  $(1/8\pi)$ . The question now mooted by Chapman was raised during the discussion of my paper. To emphasise the difference from Maxwell, and the fact that only relative results were aimed at, I at one time thought of dropping the factor  $1/8\pi$ . The idea incorporated in "magnetic activity" was, however, Bidlingmaier's, and dropping a factor which he used would inevitably have caused confusion. Also, the use of the factor made the numerical results of more convenient magnitude. I had considered the integral (6), but saw no way of utilising it satisfactorily, believing that "any complete estimate of the expenditure of energy during a magnetic storm is probably impossible." This is an opinion I still retain, though I admire the mathematical powers exhibited in the calculation which Dr. Chapman has since actually made of the energy of a magnetic storm."

Even if the integral (6) should prove, as Chapman believes, of primary importance for the calculation of the energy of a storm, the quantity integrated seems useless as a criterion of the magnetic character of a day. This is more easily seen if we write the Maxwellian integral in the form

$$(1/8\pi) \iiint (\rho^2 - \rho_0^2) dx dy dz + (1/8\pi) \iiint \rho_0^2 dx dy dz, \quad (7)$$

where

$$\rho^2 \equiv \alpha^2 + \beta^2 + \gamma^2,$$

and  $\rho_0$  is the accepted standard value.

The first integral represents the sum of Chapman's "self-energy" and "joint-energy" integrals. If, with a view to characterising the days at a particular station, we took out mean daily values of  $\rho^2 - \rho_0^2$  the result would be sometimes positive, sometimes negative, the sign even often depending on whether V was excluded or not. During some highly disturbed days, owing to contributions from different hours cutting out, the resulting mean value would resemble that of a perfectly quiet day. In an international scheme, unless we treated results from individual stations as numerical, not algebraic quantities, we should have one station neutralising another. And as the distribution of stations is perfectly haphazard, so too would be the final result. The consequences of uncertainty as to the appropriate values for  $\alpha_0$ ,  $\beta_0$ ,  $\gamma_0$ , pointed out in my previous paper in the case of "magnetic activity," would be much more serious in the case of the "joint-energy" term. An error of 1γ in the standard value adopted for any one of the elements would, in the ordinary day, swamp the contribution of the "magnetic activity" term. For the practical purposes of discriminating between different days the

superiority of Bidlingmaier's "magnetic activity" taken by itself seems hardly open to doubt.

If we aim at calculating the energy expended in a magnetic storm,\* I am disposed to agree with Dr. Chapman that the integral (6) must be taken into account, unless adequate reasons for neglecting it can be advanced. I do not, however, think that we have at present the knowledge requisite for dealing with the integral. The numerical results reached by Dr. Chapman seem to me to be determined mainly by what I cannot but consider the accident of the particular assumptions which he has made in order to obtain a definite mathematical problem capable of solution. A discussion of the more mathematical of these assumptions would be out of place here, but some remarks on the final physical assumption may be useful, especially as a possible use of the "magnetic activity" is suggested.

The value ultimately found by Chapman for his "joint-energy integral"—in comparison with which his value for the "self-energy integral" appears negligible—is"

$$H_0(\delta_e H - \delta_i H) a^3,$$

where  $a$  is the earth's radius,  $\delta_e H$  the mean value round the earth's equator of that part of the maximum depression of  $H$  due to external electric currents, and  $\delta_i H$  the corresponding depression arising from internal currents. The relation between  $\delta_e H$  and  $\delta_i H$  is obviously of fundamental importance. The following is the only explanation I notice of the choice made: "It will be assumed that one-quarter of this variation (*i.e.*, of  $\delta H_0$ ) is of internal and three-quarters of external origin. This division between the two sources is in general accordance with that which, in a study of the diurnal magnetic variations, I have found to hold good in their case."† No reference is given, but I presume reference is intended to Dr. Chapman's recent paper.‡ Referring to that source, the following is the clearest statement I can find:§ "The general result that the external field is about  $2\frac{1}{2}$  times as great as the internal field, at the earth's surface, lies between the conclusions of Schuster (... 4, approximately) and Fritsche (... 1.5 approximately); van Bemmelen obtained still lower values."

Passing by the fact that the difference between the ratios 3 : 1 and 2.5 : 1 would answer to a difference of 25 per cent. in the calculated value of the energy, the large difference between the results of different investigators, and the far from good accordance of many of Dr. Chapman's observed and

\* *Loc. cit.*, p. 77.

† *Loc. cit.*, p. 77.

‡ 'Phil. Trans.' A, vol. 218, p. 1.

§ *Loc. cit.*, p. 35.

calculated values, suggest that the potential theory is not at present capable of giving very exact information as to the character of the regular diurnal variation, even within that portion of the earth's surface represented by Dr. Chapman's observations. All but four of his stations lay between  $53^{\circ}$  N. and  $44^{\circ}$  S., the two extreme being Pavlovsk  $60^{\circ}$  N., and Laurie Island  $61^{\circ}$  S. A less favourable opinion has been recently expressed by Miss A. van Vleuten\* after an independent investigation of the problem, similar in comprehensiveness to Dr. Chapman's.

But, so far as I am aware, the results of all the investigators mentioned above, and one or two others mentioned by Miss van Vleuten, have referred to the regular diurnal variation on ordinary or quiet days. Even in comparatively low magnetic latitudes, *e.g.*, at Kew and Agincourt, the diurnal inequality in  $V$  is largely increased and modified on disturbed days. This is significant, in view of the explanation suggested by Dr. Chapman in the 'Philosophical Transactions,'† of why van Bemmelen's value for the ratio between the external and internal fields approached unity. In really high magnetic latitudes, judging by Antarctic results which there is no reason to suppose abnormal, the regular diurnal variation on highly disturbed days is almost of a different order of magnitude from that on quiet days. Until we have high latitudes adequately represented, we cannot judge whether a potential will give the regular diurnal variation there either for quiet or for disturbed days. Still less can we judge whether, if potentials apply in both cases, the ratio between the contributions from the external and internal fields will be the same for the two.

Finally, even if we knew that a potential gave the regular diurnal variation all over the earth on disturbed days, we should not be justified without further enquiry in assuming that the ratio between the external and internal fields deduced from it applied to disturbance as a whole.

It seems to me that the assumption

$$\delta_e H = \delta_i H$$

would be no more arbitrary, and even more simplifying, than the assumptions actually made by Dr. Chapman. At the present moment, and I suspect for some time to come, any positive disproof of such a hypothesis would be very difficult.

If we made this assumption, and accepted Dr. Chapman's mathematical formulæ, only the "self-energy" would survive in the energy integral, and

\* 'Koninklijk Nederlandsch Meteorologisch Instituut,' No. 102 (specially p. 112).

† *Loc. cit.*, p. 14.

the final result would depend simply on  $(\delta_e H)^2 \times (\text{volume between earth and external current sheet})$ .

If we supposed the maximum mean hourly value from N, W and V combined at Eskdalemuir in Table VII to be the mean value for the space between the earth and a concentric surface at the supposed altitude, 100 kilom., of the overhead currents, we should obtain for the space integral of the "magnetic activity" throughout this volume  $0.4 \times 10^{20}$  ergs, the precise value obtained in Dr. Chapman's equation (20) for his "self-energy integral." This is, of course, a pure coincidence.

§ 8. The phenomena described in the present and my previous paper are not favourable to the view that any very simple general theory of magnetic storms is likely to add directly much to our knowledge. In the storms we have discussed the large increase in the disturbance as we travel the comparatively short distance from Kew to Eskdalemuir suggests a principal source much nearer than the pole of the zonal harmonic of the Gaussian potential, while the large difference between Kew and Agincourt is far from suggesting symmetry round the axis of the harmonic. Something may, I think, be learned from the consideration of auroral phenomena. Magnetic and auroral phenomena do not, it is true, show a strictly proportional development. Those who have compared magnetic records from high latitudes with aurora have found that times of brightest aurora and times of largest magnetic disturbance by no means always coincide. It has been inferred that bright aurora is dependent on the concentration of electric current at a height where the atmospheric conditions favour luminosity. These currents no doubt cause magnetic disturbance, but their influence may be less than that of other currents, whether at a lower altitude or more generally distributed. Still, when a large magnetic disturbance occurs, aurora generally proves to have accompanied it, and for aurora to be seen in southern England unaccompanied by a magnetic storm is almost, if not quite unprecedented. Whilst the well-known diagram of auroral frequency, due to Fritz, may well want revision in view of more recent knowledge, its main indications are presumably reliable. They indicate a zone of maximum frequency whose largest diameter is from  $30^\circ$  to  $40^\circ$ . When we superpose magnetic data from a large number of storms, commencing at all hours of the day, we may get phenomena roughly symmetrical round the centre of the auroral zone, but any such symmetry seems improbable on a given occasion. Aurora itself certainly shows no such symmetry. At a given instant it is usually concentrated in a particular part of the heavens, and in the northern hemisphere often extends much to the south of the auroral zone. Supposing magnetic disturbance mainly due to the concentration of electric currents in one definite region of

the auroral zone, it is the distance from that region, not from the centre of the zone, that is likely to be the all-important thing. It will make all the difference to a particular station whether the concentration of current is on the near or the remote side of the zone. From this point of view, the most promising way of extending our knowledge is to compare individual records from a series of stations lying roughly on a north-south line, and so not differing much in local time. A station in the extreme north of Scotland or in the Orkneys or Shetlands would seem likely to add much to our knowledge.

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*On the Inter-crystalline Fracture of Metals under Prolonged  
Application of Stress (Preliminary Paper).*

By WALTER ROSENHAIN, B.A., D.Sc., F.R.S., and SYDNEY L. ARCHBUTT, F.I.C.  
(both of the National Physical Laboratory).

(Received March 13, 1919.)

[PLATES 1-3.]

The authors have recently made a series of observations on some cases of inter-crystalline fracture in various metals, occurring as the result of the prolonged application of stress. In explanation of these phenomena they have formulated an hypothesis which appears to afford a satisfactory account of the present observations and to correlate them with other well-known phenomena whose exact nature has, however, hitherto remained obscure. In putting their observations and hypothesis on record at the present stage, the authors are well aware that much fuller experimental investigation of the whole subject is required, and they hope to carry this forward. The evidence now available, however, appears to them to justify preliminary publication, especially in view of the fundamental interest and great practical importance of the subject.

The present paper relates to a group of phenomena some of which have long been known, in the case of brass, as "season cracking." Brass articles which have been manufactured by a process of alternate cold-working and annealing—such, for instance, as cartridge-cases and other articles made by operations of cupping and drawing—sometimes exhibit a tendency, after a period which may vary from a few hours to several years, to undergo spontaneous cracking. The occurrence of this type of failure of brass has

been a serious manufacturing difficulty and much study has been given to the subject; as a result, modifications of both the annealing and the drawing processes have been made, which, to a considerable extent, eliminate the trouble. A satisfactory explanation of "season cracking" has not, however, been put forward so far as the authors are aware. From the present point of view, perhaps the most interesting fact which has been observed about "season cracking" in brass is that the fracture—in those cases where its path can be traced clearly among the micro-constituents of the metal—markedly follows the inter-crystalline boundaries. An example of such a crack is illustrated, under a magnification of 100 diameters, in fig. 1, where the inter-crystalline character of the fracture can be clearly traced (Plate 1).

The other phenomena, recently observed by the authors, which have led up to the present study of the subject, have been met with primarily in an alloy of aluminium containing both zinc and copper. Further, fractures observed in such widely different metals as lead and mild steel (boiler plate) show features which appear to be closely related to the same subject. In the aluminium alloy referred to it has been found that when the material, after being rolled into sheets, has been subjected to a certain degree of annealing—which the authors describe as "over-annealing"—it displays a tendency to undergo a peculiar type of fracture which bears a striking resemblance to "season cracking."

If a strip of this aluminium alloy in the "over-annealed" condition is tested in a tensile testing-machine in the ordinary way, it shows no specially abnormal properties, being merely a little harder and less ductile than when correctly annealed. If a strip of the alloy is bent to a curve of moderate radius it springs back when released although it does not become quite straight again. If such a strip is held in the bent position by wrapping a piece of wire around it, the tension on the wire is at first fully maintained. After a period of time, however, which may vary, according to the degree of "over-annealing" to which the specimen has previously been subjected, from a few minutes to four days or longer, such a bent strip breaks at or near the sharpest part of the bend, the fracture being generally accompanied by many fine ramifying cracks. Microscopic examination shows quite clearly that this fracture and the accompanying cracks are strictly inter-crystalline. A typical example is illustrated in fig. 2, under a magnification of 150 diameters.

The close analogy between the fracture of such a bent strip of aluminium alloy and that of an article of cold-drawn brass is readily understood when it is borne in mind that a cold-drawn article necessarily exists in a state of great internal stress. Thus one need only imagine the bent strip of alloy to be bent into the form of a complete circle and the two ends united in

that position, to arrive at a shape produced by cold-working and holding large internal stresses. Similarly, a cup drawn from a flat sheet or from a shallower cup, may also be regarded as made up of a number of bent radial strips held together in that position, each strip being heavily "sprung." The analogy is completed by the observation that cup-shaped spinings made of the aluminium alloy in the "over annealed" condition undergo the same type of spontaneous inter-crystalline fracture as that described above.

In the case of lead, observations have been made on the sheathing of a small electric cable which failed after several years' service, by fissuring of the lead sheath.\* Examination shows that parts of the lead sheathing are badly cracked, the cracks clearly following the inter-crystalline boundaries. Their appearance is shown in fig. 3, under a magnification of 20 diameters. The similarity between this case and the two previously mentioned resides principally in the unusual type of fracture—since inter-crystalline fissures are particularly remarkable in so ductile a metal as lead. The evidence for the presence of stress is not so clear in this instance, except that the separation of various parts of the material indicates that there must have been forces at work tending to pull the material apart. The appearance of the lead crystals, however, shows that the forces at work must have been small, since the crystals themselves show no signs of having been deformed. It is quite probable that a small amount of stress was put on this cable in the process of laying, or subsequently by the effects of thermal expansion.

Finally, in a certain number of cases of failure of mild steel boiler plates, abnormal types of fracture, following the crystal boundaries have been observed.† An example of a fracture of this kind is illustrated in fig. 4 under a magnification of 500 diameters. In this case the material, forming part of a large boiler has been exposed to stress for a long time. Like the three other materials already referred to, this steel when broken in an ordinary test shows the usual fracture running across the crystals and avoiding the crystal boundaries in a systematic manner.

Having recognised the essential similarity between these various examples of metal which have failed by inter-crystalline fracture occurring *after the*

\* The sample of cracked lead cable sheathing to which the authors' observations refer was brought to their notice by Mr. L. Archbutt, F.I.C., of Derby, who drew their attention to the inter-crystalline character of the fissures. They have since found other examples of this type of failure, and are informed that it is not uncommon in lead-covered cable, where this is allowed to hang in catenaries between supports.

† A good example is described in Departmental Paper No. 231, 1910, on a "Report by the National Physical Laboratory on Some Unusual Defects in the Plates of Two Combustion Chambers on Board a Foreign-going Passenger Steamship," submitted by the Marine Department, Board of Trade.



*lapse of time*, the authors now suggest an explanation which, they believe, furnishes a rational account of the mechanism of this type of fracture and correlates the phenomena with one another and with other known facts. They have not yet had time to carry out more than a few of the test experiments which their view suggests, but so far as they have gone, the evidence appears to be entirely consistent with the explanation put forward.

The view has been held for some time by a number of metallurgists,\* and has been particularly advocated by one of the authors† that a thin layer of amorphous metal, in a state corresponding to that of a greatly under-cooled liquid, exists between adjacent crystals in any crystalline aggregate, and especially in metals. A considerable amount of evidence has been advanced in support of that hypothesis, including, particularly a series of experiments made in 1912-13 by one of the authors and D. Ewen.‡ These are of special interest in the present connection.

The manner in which fracture under an externally applied stress will occur in a crystalline aggregate held together by an amorphous inter-crystalline cement must depend on the relative physical properties of the crystals and the cement. If the cement is of the nature of an under-cooled liquid far below its freezing point such "liquid" will be in an extremely viscous condition, in that respect resembling such a substance as glass. Towards loads applied at the rates employed even in very slow tensile testing such a substance will behave like a solid of apparently high elastic

\* The conception that metal can be partially converted into an amorphous or vitreous condition by straining or polishing is due to Beilby, whose papers include: "Surface Flow in Crystalline Solids," 'Proc. Roy. Soc.,' A, vol. 72, 1903; "The Hard and Soft State in Metals," 'Faraday Soc.,' 1904, and 'Phil. Mag.,' August, 1904; "The Hard and Soft State in Ductile Metals," 'Proc. Roy. Soc.,' A, vol. 78, 1907; and "The Hard and Soft State in Metals," 'Journ. Inst. Metals,' No. 2, 1911, vol. 6. The further conception that amorphous layers exist between the crystals of unstrained metal first occurs in the following papers:—F. Osmond, Discussion on "Transformations of Steel within Limits of Temperature Employed in Heat-Treatment," 'Journ. Iron and Steel Inst.,' No. 2, pp. 61-3 (1911); G. D. Bengough, "A Study of the Properties of Alloys at High Temperatures," 'Journ. Inst. Metals,' No. 1, vol. 7, pp. 176-7 (1912); W. Rosenhain, Discussion on above; Rosenhain and Ewen, "Inter-crystalline Cohesion in Metals," 'Journ. Inst. Metals,' No. 2, vol. 8 (1912); *ibid.*, vol. 10 (1913); Rosenhain and Humfrey, "The Tenacity, Deformation, and Fracture of Soft Steel at High Temperatures," 'Journ. Iron and Steel Inst.,' No. 1 (1913); J. C. W. Humfrey, "The Inter-crystalline Fracture of Iron and Steel," 'Iron and Steel Inst., Carnegie Scholarship Memoirs,' 1911; *Idem.*, "Influence of Inter-crystalline Cohesion upon the Mechanical Properties of Metals," 'Iron and Steel Inst., Carnegie Scholarship Memoirs,' vol. 5 (1913).

† Rosenhain. See papers cited above, also "Metals, Crystalline and Amorphous." Paper before Section B, British Association, 1913, 'Engineering,' September, 1913.

‡ Rosenhain and Ewen. See papers cited in note \* above.

limit. The crystals, on the other hand, are capable of undergoing deformation by slip under relatively light stresses. Deformation and fracture will therefore occur by rupture of the crystals themselves and not by any tearing away of adjacent crystals from one another. This is in fact the type of fracture met with under ordinary conditions in all metals in a normal condition, *i.e.*, in the absence of impurities which are known to exist in the form of weak and brittle membranes along the crystal boundaries.

On the other hand, an amorphous cement of the nature of an under-cooled liquid will become rapidly less viscous—and consequently less resistant to displacement and rupture—with rising temperature. By the time that the freezing point of the metal is reached, this liquid will no longer be under-cooled, and will have the full mobility of the ordinary molten metal. From this condition the viscosity of the liquid will increase continuously, and over a certain range very rapidly, until extreme viscosity is reached at very low temperatures.

In other words, the under-cooled liquid may be expected to exhibit a large temperature-coefficient of viscosity. This is, of course, well known to be so in the case of glass. Now, there is no reason to believe that the physical properties of solid crystals undergo any very rapid change with rising temperature; even at their own freezing point they possess a considerable degree of strength and hardness. It follows from these considerations, as has been pointed out by Rosenhain and Ewen (*loc. cit.*), that at some temperature between the ordinary temperature and that of the freezing point of the metal, the relative behaviour of the crystals and the cement in a crystalline aggregate exposed to stress will be reversed, so that at any temperature above that point the cement will offer less resistance to displacement than the crystals, so that if the metal is fractured under these conditions, a purely inter-crystalline fracture will result.

This inference has been very fully verified by the experiments of Rosenhain and Ewen already referred to. They produced entirely inter-crystalline fractures, unaccompanied by any deformation of the crystals, in a number of very pure metals—including lead, gold, aluminium, tin, and others—at temperatures some degrees below their melting points. For the present purpose, however, it is important to bear in mind that the authors named worked with light loads and did not very fully consider the time factor in such experiments. When these factors are taken into consideration, the conclusion is indicated that if higher stresses had been used, and if they had been allowed to act for a longer time, similar inter-crystalline fracture would have taken place at considerably lower temperatures. A case in which this conclusion has been fully verified is provided by the experiments of Rosenhain

and Humfrey,\* in which the deformation and fracture of a very mild steel has been investigated, both by physical measurements and by microscopic observation when gradually broken in tension at temperatures above the upper critical point—i.e., above 900° C. There, it has been shown that, where crystals of  $\gamma$ -iron are held together by an amorphous cement at a high temperature, and therefore probably of relatively low viscosity, both deformation and fracture are essentially inter-crystalline, while the process of deformation is found to follow a law which at once suggests the presence of viscous flow. When it is remembered that  $\gamma$ -iron just above  $A_{c3}$  is still some 600° C. below its melting point, it will be realised that there need be nothing surprising in meeting with similar phenomena in brass or in an aluminium alloy at the ordinary temperature.

The explanation of the inter-crystalline fracture of certain metals resulting from prolonged exposure to stress which the authors desire to put forward for consideration may, then, be stated as follows:—That the constituent crystals of a metal are held together by an amorphous inter-crystalline cement, which, in some metals at all events, is sufficiently mobile to yield to the tendency of any applied stress to produce flow. In such cases it would follow that inter-crystalline rupture must occur, after the lapse of sufficient time, as the result of the prolonged action even of small stresses which may arise either from externally applied forces or from elastic deformations and consequent internal stresses. It would seem, at first sight, that such an explanation covers too much, since it would suggest the probability that inter-crystalline failure would ultimately occur in all metals as the result of prolonged exposure to stresses far below their ordinary breaking stresses. Experience clearly indicates that this is not the case, since metal structures of various kinds are known to have withstood considerable and continued stresses for very long periods. Cases of “season cracking” are in fact rather exceptional and isolated. This consideration shows that the explanation, as stated above, is incomplete, and the authors believe that the completion is to be found in a consideration of the conditions existing at a crystal boundary where a tendency exists for gradual flow of the “cement” under prolonged application of stress.

It is at once obvious that flow sufficient to cause rupture cannot occur at a crystal boundary unless the shape of that boundary and of other adjacent boundaries is favourable to movement. If, for instance, the crystals were thoroughly dovetailed into one another, rupture along the boundaries could not occur at all, even if there were no adhesion whatever between adjacent crystals. Although such a dovetailed, truly “interlocked,” structure is not

\* Rosenhain and Humfrey, *loc. cit.*, see note (\*), p. 58.

met with in metals, there are wide differences in the character of the crystal boundaries in various cases, and most notably between the crystals of the same metal in different conditions of thermal and mechanical treatment. One of the authors has recently pointed out\* that, in a metal which is undergoing more or less rapid recrystallisation or crystal growth, the crystal boundaries are notably irregular—sometimes even jagged or serrated. When crystal growth has come to an end under the conditions to which the metal is exposed, on the other hand, it is found that the crystal boundaries become smooth and tend towards rectilinear, polygonal forms. That such a process of filling up and smoothing-out of irregularities should occur is in conformity with what would be anticipated from the point of view of the energy-content of the boundaries. Whether such energy-content be ascribed to the presence of an amorphous film, or merely regarded as "surface energy," diminution of the area of these inter-crystal surfaces will diminish the amount of energy stored in boundaries. Nor need it be supposed that it is only the coarser irregularities of the boundaries which come into play in the present connection. Since crystal-growth in solid metals is known in many cases to take place by a process in which the growing crystal thrusts out arms or projections into its neighbours, it follows that the surface of a growing crystal is likely to be covered with minute irregularities—small projections thrusting forward towards or into the neighbouring crystals, but always, according to the present hypothesis, with a film of amorphous material interposed. Such projections can only maintain themselves so long as the crystal is growing at a rate which is relatively rapid in comparison with the tendency for irregularities of crystal outline to become smoothed out, so that—as the crystals cease to grow—we may expect their outlines to become both microscopically and—probably—ultra-microscopically smoother.

The part which even minute surface irregularities in the crystal boundaries may play in hindering, or even in entirely preventing movement by viscous flow of the inter-crystalline film, may, perhaps, be better understood by the aid of a rough analogy. If we have, as in fig. 5A, two smooth metal plates lying one upon the other, with a film of thick oil between them, a very slight pull will cause a displacement of one over the other, since here the viscosity of the oil is unaided, so far as resistance to motion is concerned, by any other factor. This is the case corresponding, in principle, to the very smooth crystal boundary with its interposed amorphous film. On the other hand, if the metal plates have on their surfaces even minute projections, such as are indicated in the second diagram (fig. 5B), then the resistance to relative

\* Rosenbain, Discussion on paper by Z. Jeffries on "Grain Growth," 'Journ. Inst. Metals,' No. 2, vol. 20 (1918).

motion of the plates over one another must necessarily be very much greater. If the projections are large enough to come into actual contact<sup>a</sup> by mutual

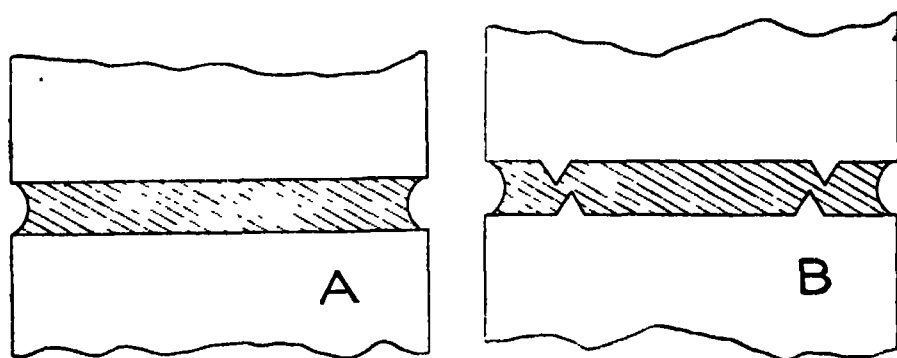


FIG. 5.

sliding of the two surfaces, then any further movement by viscous flow alone will become quite impossible, and can only occur by the actual shearing of these projections. But, as these would be numerous, this would imply the application of a stress large enough to bring about serious deformation of the crystals, and would at once lead to an entirely different type of fracture from that under discussion.

The inference that—if the authors' view of the nature of inter-crystalline fracture under prolonged loading is correct—such fracture should only occur where the crystal boundaries have assumed smooth and regular outlines, is strongly supported by the authors' observations. In the first place, the phenomena of inter-crystalline fracture in the aluminium alloy only occur when the metal has previously undergone relatively drastic annealing. Thus it is found that, when this alloy is softened by annealing at 250° C. or lower, the material shows no tendency to "season cracking." After annealing at higher temperatures the phenomenon makes itself apparent, the time required to bring about inter-crystalline fracture under bending stress decreasing from four days after annealing at 300° C. down to an hour or less after annealing at 450° C.—an exposure of one hour to the temperatures named being given in each case. Microscopic examination of the material after each of these treatments serves to confirm the inference drawn above. After annealing at 250° C. the crystals show no considerable amount of growth, and retain the irregular elongated outlines given to them by the previous rolling operation. On the other hand, after annealing at 450° C., when the "season cracking" phenomenon is most fully developed, the crystals have attained considerable size, no longer show signs of their former elongated shapes, and exhibit extremely smooth and regular boundaries.

The typical character of the crystal boundaries in this alloy in the two conditions described is illustrated in figs. 6 and 7 under a magnification of 150 diameters (Plate 3).

In this connection the authors have made a further observation of some interest. They find that, by adding to this aluminium alloy a small quantity of manganese (not more than 0.5 per cent. is required), the entire phenomenon of "season cracking," even after annealing for six hours at 450° C., disappears. Microscopic examination at once serves to correlate this fact with the inference discussed above, since it is found that the alloy containing manganese does not undergo recrystallisation at anything like the rate met with in the alloy free from manganese. The size and shape of the crystals, and the irregularity of boundary which is seen in the "pure" alloy when annealed at low temperatures (250° C. and below), is still found in the alloy containing manganese even after annealing at 450° C. This observation, therefore, serves to establish the connection between irregularity and incomplete growth of crystal boundaries and resistance to inter-crystalline fracture, which the authors' hypothesis suggests.

Evidence of the same kind is obtained by observations made on the examples of inter-crystalline fracture found in the case of lead and mild steel. In the case of the lead, already referred to above, examination shows that cracking has only occurred in patches, the remainder of the lead being perfectly sound. When the lead is etched with dilute nitric acid, it becomes perfectly evident that, in the regions where inter-crystalline fracture has taken place, the crystals have assumed a smooth regular formation, such as is characteristic of crystals which have approached an equilibrium condition—*i.e.*, in which rapid growth has ceased. Elsewhere in this same specimen, the crystals show the ragged, almost feathery, edges typical of lead crystals in process of active growth.\* The difference in type is clearly illustrated by comparing the photograph (fig. 2) with that shown in fig. 8, which shows, under a magnification of 20 diameters, a region found in the same specimen having very irregular crystal boundaries. The authors suggest that this difference of character, coupled with the fact that, where the crystals have irregular boundaries, there are no signs of failure, provides a considerable degree of support for their views.

In mild steel, examples of inter-crystalline failure are very rare, but they have been met with in several cases in steel boiler-plates which have been found badly cracked near their edges about the rivet holes. On examination, these cracks were found to be typically inter-crystalline. An example has already been illustrated (fig. 4). Careful study of several cases has shown

\* Ewing and Rosenhain, 'Phil. Trans.,' A, vol. 195, pp. 279-301 (1900).

that failure of this type is associated with a particular kind of heat-treatment of the steel, viz., prolonged annealing or very slow cooling through the

FIG. 8.

temperature range just below the lowest critical point of the steel ( $A_{r1}$ ). This treatment results in the aggregation of the cementite or iron-carbide of the steel into the form of solid globules or membranes, instead of leaving it distributed in the relatively diffuse form of pearlite more usually found in steel. This distribution of the carbide is, in itself, undesirable, and causes weakness, more particularly under impact. In the form of pearlite also, with its minutely irregular outline, the carbide would serve as a much better "key" to hinder relative motion of the crystals than it could do in the form of smooth plates or membranes. Beyond this, however, it is important to note that the heat-treatment which produces this peculiar distribution of the carbide also allows the iron or "ferrite" crystals to approach an equilibrium condition in which further growth is very slow, and which is characterised by very smooth and regular crystal outlines. We thus see the characteristic feature required by the authors' explanation reproduced in a striking manner in an aluminium alloy, lead, and mild steel, in samples all of which exhibit the phenomenon of inter-crystalline fracture following upon prolonged exposure to stress.

Another fact of interest in this connection is the effect which even a small rise of temperature appears to exert on the phenomenon of "season cracking,"

an effect which, in the authors' view, would be anticipated as a result of the rapid diminution of the viscosity of an under-cooled liquid with rise of temperature. In the case of brass, it is well known that failure from this cause is more likely to occur in a hot climate than in a cold one; it has been found that the cracking of cartridge cases, for example, is more liable to occur when goods are stored in India than with those kept in England, while the brass-work of gasoliers, exposed to the heated air in the upper part of a gas-lighted room, is particularly liable to this type of failure. In the case of lead, the ordinary temperature is so near its melting point that the metal undergoes spontaneous annealing (*i.e.*, recrystallisation) at the ordinary temperature. For such a metal, the ordinary temperature may well be regarded as "high." In the case of mild steel, although the temperature is still very far away from its melting point or even its softening point, it is at least suggestive that the cases of inter-crystalline fracture observed by the authors have in every instance occurred in the plates of steam boilers working under a high pressure and, therefore, at a correspondingly high temperature, rising in some cases up to 200° C. In the case of the aluminium alloy, the effect of a rise of temperature has not yet been investigated. The alloy, however, is one which rapidly becomes soft and weak with rising temperature—a softening which is appreciably lessened by the addition of manganese, whose powerful effect on the "season cracking" phenomenon has already been described. The effects of temperature, as a whole, however, so far as they are known, appear to be entirely consistent with the authors' view, that this type of inter-crystalline fracture results from a gradual yielding or "flow" of the viscous inter-crystalline amorphous cement, since the viscosity of such a cement would rapidly diminish with rising temperature. In the case of glass, it has recently been shown\* that at a temperature where slight softening becomes noticable, every rise of 8° C. reduces the viscosity by one half.

In the case of the aluminium alloy, the authors have made some preliminary measurements of the time required to produce rupture under various intensities of loading. The results, examples of which are given in the subjoined Table, indicate clearly that the time required to produce rupture

Tensile stress per square inch.	Time taken to produce rupture.
tons.	secs.
16	9
14	31
13	56

\* Twyman, 'Journal Soc. Glass Technology,' vol. 1, No. 1, May, 1917.



increases very rapidly with decreasing intensity of stress, in the manner which would be anticipated in a case of viscous flow. More numerous observations are, however, required to establish any definite relationship.

In these tests there is little or no elongation of the specimen. If a similar test-piece of the same material is tested in the ordinary way, it shows a breaking stress of 24 tons per square inch and an elongation of 8 per cent. on 2 inches.

Having put forward the evidence so far available in support of their explanation of the mechanism of inter-crystalline fracture, the authors wish to consider briefly some of the main objections to their views which have presented themselves.

The first of these difficulties relates to the fundamental question whether an amorphous inter-crystalline cement can or does exist. The evidence for and against this has been fully discussed elsewhere;\* here, it need only be said that until other methods of investigation become available, any *direct* proof of the existence of the cement can hardly be hoped for. On the other hand, the increasing number and range of phenomena which the hypothesis of an amorphous inter-crystalline cement serves to explain and correlate furnishes important indirect evidence in favour of the validity of the hypothesis. From that point of view, the case appears to be considerably further strengthened by the observations described in the present paper.

Perhaps the most serious difficulty which confronts the authors' views is that of accepting the somewhat novel idea that a sufficient degree of mobility can exist in the under-cooled liquid forming the inter-crystalline cement to allow of viscous flow resulting in fracture at temperatures not very much above the ordinary. On this point it may be said that we have no data as to the viscosity of under-cooled metal, and can only judge by analogy with other substances, such as glass. But while glass is very readily under-cooled, this is not the case with metal, which has not been experimentally under-cooled in any considerable quantity sufficiently far below the freezing point to save it from spontaneous crystallisation. This difference may well be due to a difference in regard to viscosity—that while glass when under-cooled at once increases so rapidly in viscosity that crystallisation soon becomes impossible, in metals the rapid rate of increase of viscosity may not begin until a much lower range of temperatures is reached, with the consequence that a degree of under-cooling which could easily be achieved experimentally is not sufficient to retain the material in a "vitreous" condition. If this is the case then at temperatures not far above that of the air, the inter-crystal cement might be sufficiently mobile to yield very slowly to the prolonged effects of stress.

\* Rosenhain, see papers cited in note, p. 58.

It may further be pointed out that in the case of  $\gamma$ -iron, Rosenhain and Humfrey (*loc. cit.*) have shown definite evidence of viscous flow taking place in the crystal boundaries. Yet  $\gamma$ -iron at a temperature just above  $900^{\circ}$  C. is still  $600^{\circ}$  C. below its melting point. As compared with this, brass, lead and the authors' aluminium alloy at the ordinary temperature are approximately some  $900^{\circ}$  C.,  $300^{\circ}$  C., and  $600^{\circ}$  C. below their respective melting points. Their relative conditions, therefore, need not be regarded as essentially different; if viscous flow in the amorphous cement can be accepted in the one case, there need be no great difficulty in extending the conception to the others.

The mild steel referred to above in connection with inter-crystalline failure in boiler plates is, however, in a somewhat different position, since at the ordinary temperature this is some  $1500^{\circ}$  C. below the melting point of iron, so that even a rise of some  $200^{\circ}$  C. in a high-pressure boiler does not bring it into the same range as aluminium or brass. The explanation may, however, lie in the allotropic transformations which iron undergoes. The melting point near  $1500^{\circ}$  C. is that of  $\gamma$ -iron, or possibly of some other modification stable at those very high temperatures. The iron which undergoes inter-crystalline fracture, however, is  $\alpha$ -iron. If this variety could be prevented from passing into the other modifications on heating, it seems probable that its melting point might lie not very far above the transformation temperature. At all events, the variations of the physical properties of  $\alpha$ -iron with rising temperature suggest that they are related rather to its transformation temperature, in the neighbourhood of  $900^{\circ}$  C., than to the melting point of  $\gamma$ -iron near  $1500^{\circ}$  C. If this view is tenable, the difficulty in the present connection disappears, since the transformation temperature of iron is rather lower than the melting point of brass.

If the explanation of "season cracking" and similar phenomena of inter-crystalline fracture which has here been put forward proves, on further investigation, to be well founded, consequences of considerable practical importance may be drawn from it. It would appear that the risk of inter-crystalline fracture following upon the prolonged action of stresses far below the normal "breaking strength" of the material is of very considerable importance, and that our immunity from numerous and serious failures from this cause is due to the fact that in the majority of metals as ordinarily employed the condition of the crystal boundaries is not favourable to viscous flow. In the case of certain alloys, such as steels containing moderate amounts of carbon, this safety is no doubt due to the presence of a second constituent possessing characteristically irregular outlines. In other cases, the safe character of the boundaries can only be due to the fact that as a

result of manufacturing conditions the crystals are left in a condition of incomplete growth in which they have not been able to develop smooth and regular outlines. Failures from this cause have, therefore, only arisen in a relatively few special cases where metal has been subjected to somewhat drastic annealing which has allowed the crystals to attain a condition of metastable equilibrium in which their outlines have had an opportunity of becoming smooth and regular. As has been found by practical trials in the case of brass, such "season cracking" can be prevented by a suitable modification of the annealing operations. The most serious cases, however, are those arising in steel. If these have been rightly correlated with the others, the remedy is clear—the heat-treatment of the steel must be altered in such a manner as to avoid all risk of the formation of the smooth and regular boundaries which—quite apart from any theory—are definitely associated with this dangerous type of failure. Fortunately the well-known operation of "normalising" mild steel by heating it for a very short time to a temperature just above the upper critical point, followed by rapid cooling in air, is sufficient entirely to eliminate all risk of the development of these apparently dangerous structural arrangements.

The authors gratefully acknowledge much valuable help in carrying out some of the experimental work described in this paper which they have received from several of their colleagues, particularly from Mr. F. S. Tritton. They are very specially indebted to Mr. L. Archbutt of Derby for first calling their attention to the occurrence of inter-crystalline failure in lead. They also desire to acknowledge the interest which has been taken in this research by Sir Richard Glazebrook, C.B., F.R.S., Director of the National Physical Laboratory, where the work has been carried out.

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FIG. 1.

Inter-crystalline crack in "season-cracked" brass  $\times 100$

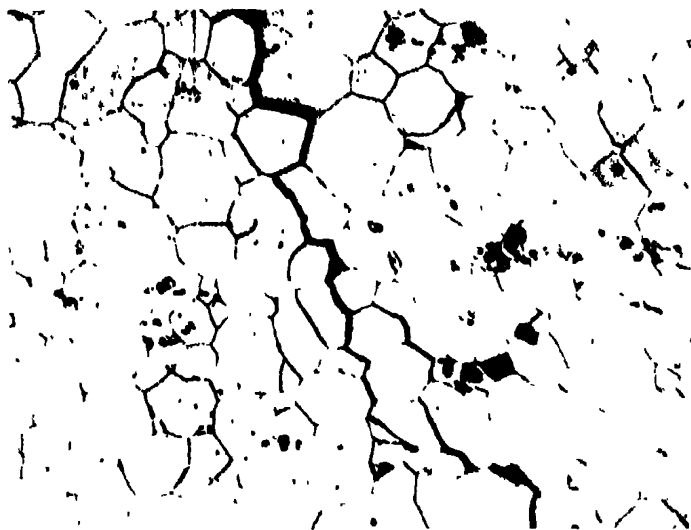


FIG. 2.

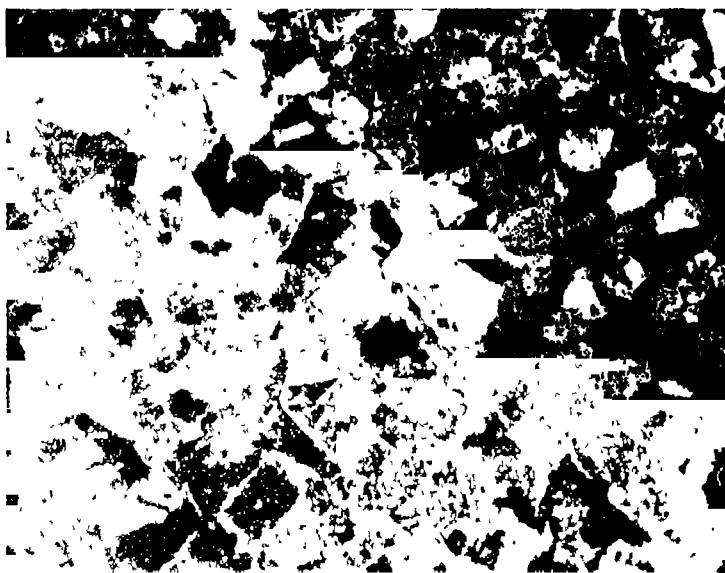


FIG. 3.



FIG. 4.



FIG. 6.

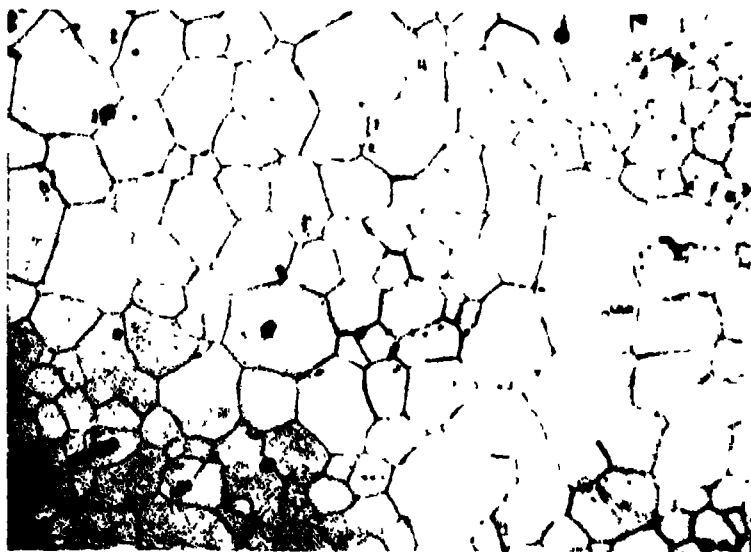


FIG. 7.



*On the Determination of the Secular Acceleration of the Moon's Longitude from Modern Observations.*

By ERNEST W. BROWN, F.R.S.

(Received March 17, 1919.)

In 'Proceedings,' Ser. A, vol. 95, pp. 300-302, Mr. Nevill applies to a set of observed errors of the Moon's longitude a change of the form  $a + bt + ct^2$  and argues that the result shows a total absence of any difference between the theoretical and observed values of the secular acceleration in the modern observations extending from 1640 to 1915. The value of  $c$  in the above expression has been so chosen that the value actually used shall be that given by theory.

If the result of the application of such a change had been the reduction of the errors to small quantities which had apparently no systematic character, there might have been some foundation for the statement, but this is far from being the fact. It has long been well known, and it is again evident from the table of values which Mr. Nevill gives, that the errors show a periodic character and are so large that no conclusions can be drawn concerning the coefficient  $c$  until the nature and quantity of their periodicity has been determined. In order to avoid misconception it should be stated that  $a$ ,  $b$  are constants which must be determined from observation and that large changes in their values are possible without sensibly affecting other portions of the theoretical expressions for the Moon's co-ordinates. Hence, it is usual in making any alteration in  $c$  to so determine  $a$ ,  $b$  that the observations are best represented by the formula.

The main question involved is that of the representation of a curve of limited length by a formula, to a given degree of accuracy. A simple illustration is furnished by the expression  $2''(t^2 - 1)$ , where the unit of time is a century and the epoch is 1800. The changes produced at 1900 and 1700 by this formula are zero and the greatest change between 1915 and 1640 is at 1800 where the change is  $-2''$ . A glance at the numbers in Mr. Nevill's column H $\alpha$  is sufficient to show at once that the application of such a formula does not alter the periodic character of the errors, and it is known for theoretical reasons that it cannot do so, as long as knowledge concerning the periodicity of the errors is absent.

The fact is that the precise value to be attributed to the coefficient  $c$  is inseparably bound up with the representation of the remaining errors so long as the principal part of these errors can be represented by a periodic term



with a period of a length similar to that covered by the series of observations. The question has been fully dealt with by Tisserand in the third volume of his '*Mécanique Céleste*.' In vol. 72, p. 708, of the '*Monthly Notices of the Royal Astronomical Society*,' I have given a complete numerical illustration, the results of which can be very briefly stated. Let

$$A = 1.88'' (t - 0.27)^2 + 12.95'' \sin(131^\circ t + 100.6^\circ),$$

$$B = 1.56'' - 1.43'' (t - 0.27) + 11.15'' \sin(138^\circ t + 99.4^\circ),$$

where  $t$  is the time reckoned in centuries from 1800. It was shown that the difference  $(A - B)$  will never exceed  $0.1''$  between 1710 and 1930 or  $0.5''$  between 1620 and 1950. Even so considerable an alteration as  $5.4''t^2$  was, by similar methods and by a proper choice of the periodic term, and of the coefficients of  $t^0, t'$ , shown to produce changes less than  $0.3''$  between 1710 and 1930 and changes less than  $1.6''$  between 1620 and 1950. Hence the coefficient of  $t^2$  cannot be obtained from the modern observations until the source of the periodic term is known and its constants determined with very considerable accuracy from the theory. Even when either  $A$  or  $B$  has been applied to the longitude, the remaining errors require for their representation at least three periodic terms with coefficients of some seconds, so that the difference between adopting  $A$  or  $B$  cannot be settled on the basis of the observations.

At the end of his paper Mr. Nevill states that the large outstanding fluctuations are due to Hansen's erroneous values for the terms of very long period, and that they disappear so soon as these are replaced by their correct values. He apparently ignores the fact that the work of Radau, Newcomb, and myself shows substantial agreement, both theoretical and numerical, in the conclusion that these outstanding errors cannot be explained in any such way. In order to justify such a statement in the absence of any published and detailed investigation of his own, it is necessary that he should show in what manner we have failed to perform our work correctly.

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# On the Area of Surfaces.

By Prof. W. H. YOUNG, Sc.D., F.R.S.

(Received March 18, 1919.)

The necessary and sufficient condition that a curve should possess a length, this length being given by the usual integral formula, is well known. The curve being defined by the equations

$$x = x(u), \quad y = y(u),$$

the condition is that  $x(u)$  and  $y(u)$  should be expressible as integrals\* with respect to  $u$ .

It may seem scarcely credible that no corresponding theorem is known with regard to the area of a surface. Such is, however, the case. And what is more surprising, no one has hitherto succeeded in giving such a definition of the area of a curved surface as permits of a determination of a sufficient condition of a general nature that the surface should possess an area, this area being given by the integral formula known to hold in the simplest cases.

The step from one dimension to two has, in this instance, as in many other parts of analysis, been found difficult to take. The reason seems to be in part, here also, that several generalisations, at first sight equally eligible, of the definition involved, and of the theorem to be proved, appear to be possible, while it has been difficult to perceive in what way the analytical reasoning employed in the one-dimensional case is capable of extension to higher space.

As the length of a curve is defined as the limit of the perimeters of inscribed polygons, it was for a long time supposed sufficient to define the area of a curved surface as the limit, assumed to be necessarily unique, of the areas of inscribed polyhedra, the faces being usually taken to be triangular. That this definition is fallacious is, however, easily seen, as was pointed out almost simultaneously† by Peano and Schwarz, even when the surface is so simple a one as a bounded portion of a cylinder of revolution. The definition only leads to a finite limit when a suitable limitation is imposed on the magnitude of the angles of the faces. Almost the only case, moreover, in

\* Absolutely convergent (or Lebesgue) integrals.—L. Tonelli, 1912, "Sulla lunghezza di una curva," *Atti di Torino*, vol. 47, 1908; "Sulla Rettificazione delle Curve," *ibid.*, vol. 43.

† About 1880. See Lebesgue's Dissertation, "Intégrale, Longueur, Aire," 1902, *Annali di Mat.*, ser. 3, vol. 7, p. 298.

which the definition based on triangulation works (even when such a limitation is imposed), is that in which the equations defining the surface are analytic, or, at any rate, the tangent plane to the surface exists everywhere, varying continuously from point to point.

Even Lebesgue, who defines the area as the lower limit of the areas of polyhedra which themselves tend uniformly\* to the surface as limit, has found it only possible to obtain the integral formula in this latter very special case. Thus, when the partial differential coefficients of  $x$ ,  $y$ , and  $z$  are not continuous, but are bounded,† he does not succeed in proving more than that the surface has an area *according to his definition*, and that this area is *not greater than* the double integral‡ with which the working mathematician expects to operate.

For the rest, Lebesgue's definition itself is not quite so simple even as might be supposed. On the one hand it is only applicable to surfaces which are the uniform limits of polyhedra; and on the other the assumption that the area is to be the *least* of certain limits, apart from its arbitrariness, raises a doubt as to whether the sum of the areas, so defined, of two portions into which we divide our surface is the same as the area of the whole. In fact, the lower limit of the sum is not in general the sum of the lower limits, and Lebesgue is consequently under the necessity of justifying his definition, which involves him in a somewhat lengthy and delicate discussion.

Among the earlier definitions of area quoted by Lebesgue, those due to Peano and Minkowski are worthy of mention; the first because it betrays real appreciation of the nature of the problem to be solved, and a fine sense of its difficulties, the second because of the paradoxical and even absurd results to which it may be said to lead.

Peano§ remarks that, given a skew curve  $C$ , we can, at least in simple cases, find a plane curve  $c$ , whose projection on each co-ordinate plane has the same area as that of the skew curve. If then the given surface be supposed capable of division into portions by means of such closed contours  $C$ , the area of the surface may be defined in terms of the sum of the areas of

\* Precisely,  $x_p(u, v)$ ,  $y_p(u, v)$ ,  $z_p(u, v)$  being the co-ordinates of a point on the  $p$ th polyhedron,  $x(u, v)$ ,  $y(u, v)$ ,  $z(u, v)$ , those of one on the surface, Lebesgue demands that  $x_p$ ,  $y_p$  and  $z_p$  should tend uniformly to  $x$ ,  $y$  and  $z$  respectively, *loc. cit.*, p. 301.

† Lebesgue proves, *loc. cit.*, §70, pp. 85 and 86, that this is the necessary and sufficient condition that every curve on the surface corresponding to a rectifiable curve in the  $(u, v)$  plane should be rectifiable. As he remarks, such a surface may cease to possess this property when the variables  $u, v$  are transformed. The property is not a property of the surface *per se*, but in part also of one of its parametric representations.

‡ "Toute définition géométrique qui ne conduirait pas à ce nombre consacré par l'usage serait en effet rejetée," Lebesgue, *loc. cit.*, p. 300.

§ 'Atti della Reale Accademia dei Lincei, Rendiconti,' 1890.

the corresponding  $c$ 's, and in Peano's statement is the upper limit of this sum. Apart, however, from certain scruples felt by Lebesgue in accepting this suggestion as a satisfactory basis, it is not known under what conditions the definition is applicable, nor, I believe, has it been shown that, even when valid, it leads to the desired formula.

Minkowski's\* definition is given by Lebesgue in a footnote without criticism. It proceeds from the point of view that the notion of volume is essentially simpler than that of surface. This is, at least, open to discussion, even if we confine our attention to areas and volumes made up of positive parts. Minkowski then describes round every point of the surface as centre a sphere of radius  $r$ , in this way tracing out a portion of space, which may be regarded as possessing a volume  $V(r)$ , and he defines the area of the surface as the limit, when it exists, of  $V(r)/\pi r^2$ . In the same way he defines the length of a plane curve, by means of an area  $V(r)$  similarly formed, as the limit of  $V(r)/2r$ . I have, however, shown that even a countably infinite set of points can be constructed to have a positive length, and even to have an infinite length, with Minkowski's definition. The peculiarities which may present themselves in higher space, and when the set of points is more than countably infinite, are evidently no less paradoxical.

§ 2. I propose in the present communication to give a brief account of a theory of the area of surfaces, which I have formulated, and which appears to me to answer to all the requisites. I begin by explaining the sequence of ideas which I at first followed.

If we actually form the summation of the areas of the triangular faces of a polyhedron inscribed in the surface

$$x = x(u, v), \quad y = y(u, v), \quad z = z(u, v)$$

—this surface being supposed to be in  $(1, 1)$  correspondence with the plane of  $(u, v)$ —namely,

$$\Sigma \{A_{r,s}^2 + B_{r,s}^2 + C_{r,s}^2\}^{\frac{1}{2}},$$

where

$$C_{r,s} = \begin{vmatrix} x(u+h_r, v+k_r) & y(u+h_r, v+k_r) & 1 \\ x(u+h_s, v+k_s) & y(u+h_s, v+k_s) & 1 \\ x(u, v) & y(u, v) & 1 \end{vmatrix}$$

we are naturally led to examine, with the object of clearing up our ideas, the simpler summations, such as

$$\Sigma |C_{r,s}|,$$

obtained by omitting the variable  $z$ . This corresponds to the problem of determining the sum, without regard to sign, of the areas of the three-point

\* 'Jahresbericht der deutschen Mathematiker Vereinigung,' 1901.

images in the  $(x, y)$ -plane of three-points in the  $(u, v)$ -plane. It at once becomes evident that even in the simplest case, in which the partial differential coefficients of  $x$  and  $y$  with respect to  $u$  and  $v$  exist everywhere and are continuous, a restriction on the magnitude of the angles in the triangulation, either in the  $(u, v)$  or in the  $(x, y)$ -plane, is necessary. Otherwise we might, for example, have a triangle of definite area in the  $(x, y)$ -plane corresponding to three points in a straight line in the  $(u, v)$ -plane.

Suppose the partial differential coefficients are all less than a fixed finite quantity. Then it is easily seen that  $C_{r,s}$ , the expression already written down for the area of the triangle in the  $(x, y)$ -plane, is less than a bounded multiple of

$$\{h_r + |k_r|\} \{ |h_s| + |k_s| \},$$

and therefore of

$$\sqrt{(h_r^2 + k_r^2)} \sqrt{(h_s^2 + k_s^2)}.$$

On the other hand, the area of the corresponding triangle in the  $(u, v)$ -plane may be written

$$\frac{1}{2} \sqrt{(h_r^2 + k_r^2)} \sqrt{(h_s^2 + k_s^2)} \sin \gamma.$$

If, then,  $\gamma$ , which is an angle of the triangle in the  $(u, v)$ -plane, lie between fixed limits  $\epsilon, \pi - \epsilon$ , the ratio of the areas of the two triangles will be a bounded one. It is then easy to deduce that with this understanding, namely, that one at least of the three angles of each of the triangles in the  $(u, v)$ -plane should satisfy this limitation, the triangulation method leads, when the partial differential coefficients exist and are continuous, to a satisfactory result. In particular, the limitation is satisfied, when one of the angles is a right angle.

§ 3. Further progress appearing to be attended with serious difficulties, I attempted to still further simplify the problem by confining my attention to *directed areas*, in the case of correspondence between two planes, not, of course, necessarily  $(1, 1)$ . The problem became, then, that of determining a directed area in the  $(x, y)$ -plane corresponding to a rectangle in the  $(u, v)$ -plane, and, more precisely, that of calculating the magnitude obtained by adding together triangles in the  $(x, y)$ -plane taken with their proper sign, and taking the limit of their sum. Depending, as this limit necessarily does, only on the form of the image in the  $(x, y)$ -plane of the perimeter of the fundamental  $(u, v)$ -rectangle, the idea is suggested that we may define the area in terms of this curve rather than in terms of portions of the plane bounded by it.

For details I must refer my readers to a communication made elsewhere. The main result I obtained in this direction was as follows:—

I define the area of a closed curve given by the equations

$$x = x(u), \quad y = y(u),$$

as the limit of the area of an inscribed polygon, whenever this limit is unique and finite for every mode of inscription, the sides being all less than a norm  $\beta$ , which tends to zero as limit. The area of this polygon is itself defined as the sum of the moments, taken each with their proper sign, about any point in the plane, of forces represented in magnitude, line of action, and sense, by the sides of the polygonal figure taken in order. In other words, the area of the curve is defined as the limit of the moment of the couple equivalent to the forces in question.

With this definition we may assert, for example, that every closed plane curve which is *rectifiable*, or, more generally, is such that one of the continuous functions  $x(u)$  and  $y(u)$  has bounded variation, has an area given by the formula

$$A = \frac{1}{2} \int \{x(u) dy(u) - y(u) dx(u)\}.$$

So far all is easy. The difficulty is to transform into a double integral the formula just written down, under certain conditions to be investigated. The result here obtained is the following:—

$$\text{If} \quad x = x(u, v), \quad y = y(u, v),$$

have partial derivatives  $\partial x/\partial u, \partial y/\partial u, \partial x/\partial v, \partial y/\partial v$  (not necessarily differential coefficients) which are bounded, or more generally are such that

$$\frac{\partial x}{\partial u}, \quad \frac{\partial y}{\partial u}$$

are, except for a set of values of  $u$  of content zero, each numerically less than, or equal to, a summable function of  $u$ , and

$$\frac{\partial x}{\partial v}, \quad \frac{\partial y}{\partial v}$$

are, except for a set of values of  $v$  of content zero, each numerically less than, or equal to, a summable function of  $v$ , then the area of the curve in the  $(x, y)$ -plane which corresponds to a rectangle in the  $(u, v)$ -plane, with sides parallel to the axes of  $u$  and  $v$ , is given by the usual formula,

$$A = \iint \frac{\partial(x, y)}{\partial(u, v)} du dv,$$

the double integral being taken over the rectangle in question.

§ 4. It should be noticed that the *raison d'être* of the concept of area, thus defined, and the formula embodying it, lie in the very nature of things. They are nothing more than the generalisation for the functional relationship

between two planes, of the well-known, and in its familiarity almost trivial, concept of *directed length*, and of the simple formula

$$x = \int \frac{dx}{du} du,$$

which, in the functional relationship between two lines, expresses it. And as no necessary and sufficient condition in terms of the integrant is known for the truth of the latter formula, it is not surprising that the condition we have obtained in two dimensions is a sufficient and not a necessary one.

None the less, it is only in the case of a simple Jordan curve, that is, a curve defined by a (1, 1) continuous correspondence with the circumference of a circle, and possessing accordingly the property of dividing the plane into two distinct portions, that a general sense has been hitherto given to the term "*area of a closed curve*," and, under suitable conditions, a formula obtained for it.

§ 5. The question at once suggests itself, whether this new concept and the formula cannot be utilised in the theory of surfaces. For this purpose we have to generalise in a suitable manner the idea of chord, or, more precisely, the number expressing the invariant property belonging to two points. The chords are directed lengths, but it is the sum of their moduli that we add. What we now want, then, is a plane vector, and we shall require to sum the moduli of a number of such vectors, just as, in defining the length of a curve, we add the numerical values of the distances between successive points. From this point of view, we have to find a plane vector whose projections on the co-ordinate planes are directed areas in those planes.

If we start with a surface defined by the equations

$$x = x(u, v), \quad y = y(u, v), \quad z = z(u, v),$$

we shall naturally divide the fundamental  $(u, v)$ -rectangle into sub-rectangles  $(u, v; u+h, v+k)$ , and we shall in this way obtain small directed areas in the  $(y, z)$ ,  $(z, x)$ , and  $(x, y)$ -planes, which are nothing less than the projections on these planes of the portions of the surface corresponding to the little  $(u, v)$ -sub-rectangles. The contour of such a portion of the surface projects precisely into the curves of which these are the directed areas. We are thus led to see that the generalisation of the length of the chord for a curve is, for a surface, the magnitude of the couple, defined as follows:—

Inscribe in the skew curve, which forms the contour of each little portion of the surface, a polygonal figure, whose sides are all less than a certain norm. If we suppose acting along the sides of this figure forces represented by the sides in magnitude, line of action and sense, these will be equivalent to a

couple. The magnitude of this couple being supposed to have a unique limit as the norm tends to zero, this limit is defined to be *the area of the skew curve*. This area is, then, the generalisation for surfaces of the concept *length of chord* in the case of a curve.

It will be remarked that, when, as we may for simplicity suppose, there is a (1, 1)-correspondence between the surface and the  $(u, v)$ -plane, these little contours on the surface necessarily divide it up into curvilinear quadrilaterals without ambiguity. Now if we suppose the little rectangles in the  $(u, v)$ -plane to be all of span less than a norm  $\beta_n$ , where  $\beta_1, \beta_2, \dots$  are successive positive quantities with zero as unique limit, and if we form the sum  $B_n$  of the magnitudes of the areas of the contours corresponding to the perimeters of these little rectangles, and if, as  $n$  increases indefinitely, this sum  $B_n$  has a unique limit, independent of the particular mode adopted in dividing the fundamental  $(u, v)$ -rectangle by lines parallel to the axes of  $u$  and  $v$ , as well as of the mode in which the norm  $\beta_n$  diminishes, this unique limit is called the area of the portion of surface in (1, 1)-correspondence with the fundamental  $(u, v)$ -rectangle.

§ 6. We now pass to the proof of the fundamental theorem, in the theory of the area of surfaces as above defined, which may be stated as follows:—

*If  $x(u, v)$ ,  $y(u, v)$ , and  $z(u, v)$  possess (first) partial derivatives with respect to  $u$ , which are, except for a set of values of  $u$  of zero content, each less than, or equal to, an absolutely integrable (summable) function of  $u$ , and if similar statements hold for their partial derivatives with respect to  $v$ , and if, further,  $x$ ,  $y$ , and  $z$  are expressible as integrals with respect to  $u$ , and as integrals with respect to  $v$ , then the surface necessarily possesses an area  $A$ . Moreover, further,*

$$A = \int_a^c \int_b^d \left\{ \left( \frac{\partial(y, z)}{\partial(u, v)} \right)^2 + \left( \frac{\partial(z, x)}{\partial(u, v)} \right)^2 + \left( \frac{\partial(x, y)}{\partial(u, v)} \right)^2 \right\}^{\frac{1}{2}} du dv.$$

*Thus, in particular, the surface has an area, and this area is given by the preceding formula if  $\partial x/\partial u$ ,  $\partial y/\partial u$ ,  $\partial z/\partial u$ ,  $\partial x/\partial v$ ,  $\partial y/\partial v$ , and  $\partial z/\partial v$ —these symbols standing for partial derivatives, and not merely differential coefficients—are bounded functions of  $(u, v)$ .*

§ 7. Let us employ the well-known formulæ for the resultant couple of a system of forces, typically represented by  $(X, Y, Z)$ , acting at the point  $(x, y, z)$ , and bear in mind that there is no resultant force, owing to the fact that each contour is a closed curve, and that, accordingly, the couple whose components are

$$\Sigma(yZ - zY), \quad \Sigma(zX - xZ), \quad \Sigma(xY - yX),$$

is independent of the choice of origin, as well as of axes. We then see, not only that the area of the typical contour has for magnitude the sum of the



squares of the areas of the projections of the contour on the three co-ordinate planes, but also that this magnitude is, in virtue of the theorem quoted in § 3,

$$= \sqrt{\left\{ \left[ \int_u^{u+h} \int_v^{v+k} \frac{\partial(y, z)}{\partial(u, v)} du dv \right]^2 + \left[ \int_u^{u+h} \int_v^{v+k} \frac{\partial(z, x)}{\partial(u, v)} du dv \right]^2 + \left[ \int_u^{u+h} \int_v^{v+k} \frac{\partial(x, y)}{\partial(u, v)} du dv \right]^2 \right\}},$$

and is therefore, in virtue of a theorem in inequalities of which the proof is indicated below,

$$= \int_u^{u+h} \int_v^{v+k} \sqrt{\left\{ \left[ \frac{\partial(y, z)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(z, x)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(x, y)}{\partial(u, v)} \right]^2 \right\}} du dv,$$

where  $(u, v; u+h, v+k)$  is the little rectangle of which the little contour is the image.

Hence the sum of the areas of all our contours, and therefore also all the limits of this sum, are

$$= \int_a^c \int_b^d \sqrt{\left\{ \left[ \frac{\partial(y, z)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(z, x)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(x, y)}{\partial(u, v)} \right]^2 \right\}} du dv.$$

Moreover, this is true whatever the process adopted for subdividing the fundamental  $(u, v)$ -rectangle by lines parallel to the axes of  $u$  and  $v$ .

§ 8. That in any one mode of proceeding by subdivision, *i.e.*, when all the dividing lines at one stage are retained at all subsequent stages, we get a unique limit is evident from the fact that the summation at each stage cannot be less than that at the preceding stage. In fact, in a further subdivision of any one sub-rectangle, we get contours on the surface whose resultant area is the area of the contour corresponding to the undivided sub-rectangle, and the sum of the areas of these contours must by repeated application of the triangle of couples be at least as great as their resultant area. We have still to prove, not merely that in two different modes of subdivision the two limits obtained are equal, but also that whatever process we adopt, by which the norm tends to zero, we obtain a unique and invariable limit.

§ 9. Let us denote by  $B$  any (variable) division, such as we have utilised, of the fundamental  $(u, v)$ -rectangle into sub-rectangles, and let the greatest of the sides of these sub-rectangles be less than a certain norm  $\beta$ . We shall use  $B$  also numerically to denote the (variable) sum of the areas of the contours on our surface corresponding to these sub-rectangles.

Let  $U$  denote the upper bound of  $B$  for all modes of division; this is certainly a finite number, since it cannot exceed our double integral.

We may, therefore, let  $C$  denote a fixed division, such that the number  $C$  differs from  $U$  by less than  $\epsilon$ , where  $\epsilon$  is a small positive quantity, chosen at will.

Then the sum of those sub-rectangles of  $B$ , which we may call  $R_1$ , each of which lies in more than one sub-rectangle of  $C$ , is less than  $\beta$  times the sum of the lengths of all the dividing lines of  $C$  in the fundamental rectangle. Thus by choosing the norm  $\beta$  relatively small enough, the sum  $R_1$  is as small as we please.

These sub-rectangles,  $R_1$ , are themselves subdivided by the lines of the fixed division  $C$ ; and the corresponding contours will therefore have for the sum of their areas a quantity as small as we please, since, as we saw, this is not greater than our double integral over these sub-sub-rectangles, that is, over  $R_1$ .

If we add to these sub-sub-rectangles the remaining sub-rectangles  $R_2$ , which with  $R_1$  constitute the division  $B$ , we get a new division  $G$  of the fundamental rectangle, where accordingly, when  $\beta$  is small enough,

$$G \leq B + \epsilon,$$

since

$$R_2 \leq B.$$

But since  $G$  is got by subdividing the fixed division  $C$ ,

$$C \leq G,$$

by what was already proved. Thus

$$C \leq B + \epsilon,$$

and therefore

$$U - \epsilon \leq B + \epsilon \leq U + \epsilon.$$

Since this is true for all variable divisions  $B$ , whose norm  $\beta$  is sufficiently small (the smallness being determined by  $\epsilon$ , and the fixed division  $C$ ), we have, if  $L$  be any limit approached by the numbers  $B$ , as  $\beta \rightarrow 0$ ,

$$U - \epsilon \leq L + \epsilon \leq U + \epsilon.$$

Since  $\epsilon$  is as small as we please

$$L = U.$$

Thus the numbers  $B$  have a unique finite limit, however the process of division be performed, when the norm  $\beta$  tends to zero in any manner, and this limit is the upper bound  $U$  of all possible numbers  $B$ .

This proves the theorem enunciated in § 6.

§ 10. From the uniqueness of the limit two essential links in the chain of reasoning follow, namely, that this unique limit may be regarded as a function of  $(u, v)$ , corresponding to the rectangle whose upper right-hand corner is the point  $(u, v)$ , and that this function is monotone ascending with respect to  $u$ ,

and monotone ascending with respect to  $v$ . Its continuity with respect to  $u$ , and with respect to  $v$ , then follows once again by the use of the fact that, in changing, for example, from  $u$  to  $u+h$ , we have merely to add on the value of the limit for the whole vertical strip between the values  $u$  and  $u+h$ , and therefore, by the inequality obtained in § 7, and the property of an integral, tends to zero as  $h \rightarrow 0$ . Hence, or similarly, it follows that this function is a continuous function of  $(u, v)$ , and monotonely monotone.

It now follows that the double increment of this function, which we may call  $Q(u, v)$ , being equal to the value of the limit corresponding to the rectangle  $(u, v, u+h, v+k)$ , is not less than the area of the corresponding contour, that is, it is

$$\geq \sqrt{(H_1^2 + H_2^2 + H_3^2)},$$

where

$$H_1 = \int_u^{u+h} \int_v^{v+k} \frac{\partial(y, z)}{\partial(u, v)} du dv,$$

and  $H_2$  and  $H_3$  as got from this by cyclical change of  $x, y$ , and  $z$ .

Hence any repeated derivate of  $Q$  is not less than the corresponding repeated limit of

$$\frac{1}{hk} \sqrt{(H_1^2 + H_2^2 + H_3^2)},$$

that is, of

$$\geq \sqrt{(H_1/hk)^2 + (H_2/hk)^2 + (H_3/hk)^2}.$$

But  $H_1/hk$ , being the double incrementary ratio of a certain double integral, has the integrant  $\partial(y, z)/\partial(u, v)$  for repeated limit, except for a set of values  $(u, v)$  of content zero. Hence, except at such a set of content zero,

$$\frac{\partial^2 Q}{\partial u \partial v} \geq \sqrt{\left\{ \left[ \frac{\partial(y, z)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(z, x)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(x, y)}{\partial(u, v)} \right]^2 \right\}}.$$

But  $Q(u, v)$  is monotonely monotone ascending with respect to  $(u, v)$ , and is therefore not less than the double integral of its repeated derivatives, which necessarily coincide and are finite, except at a set of content zero. Hence

$$Q(u, v) \geq \int_a^u \int_b^v \sqrt{\left\{ \left[ \frac{\partial(y, z)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(z, x)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(x, y)}{\partial(u, v)} \right]^2 \right\}} du dv.$$

But, by § 7,  $Q$  is not greater than the double integral. Therefore

$$Q(u, v) = \int_a^u \int_b^v \sqrt{\left\{ \left[ \frac{\partial(y, z)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(z, x)}{\partial(u, v)} \right]^2 + \left[ \frac{\partial(x, y)}{\partial(u, v)} \right]^2 \right\}} du dv,$$

which proves the theorem of § 6, by putting  $u = c, v = d$ .

[N.B.—The analogy with one dimension is complete. The summations in each division being there also increased when we put in additional chords.]

§ 11. We now prove the theorem on inequalities utilised above.  
Theorem.

$$\left[ \left\{ \int_a^b f(x) dx \right\}^2 + \left\{ \int_a^b g(x) dx \right\}^2 + \left\{ \int_a^b h(x) dx \right\}^2 \right]^{\frac{1}{2}} \\ = \left[ \int_a^b \{ [f(x)]^2 + [g(x)]^2 + [h(x)]^2 \} dx \right]^{\frac{1}{2}},$$

where  $x$  stands for any finite number of variables, and the integral represents the corresponding multiple integral.

Note, moreover, that the theorem remains true, if there be any finite, or countably infinite, set of functions,  $f, g, h, \dots$  taken instead of only three as in the enunciation. The argument does not depend on the number of functions, when this is finite, and the case when it is infinite follows from the finite case, by a familiar process, whenever the limit on the right-hand side is finite, and when it is infinite the statement is equally true.

§ 12. To prove this theorem it is sufficient to suppose the functions each to possess only a finite number of values, these values being assumed on a finite number of rectangles, or intervals in the generalised sense. The result stated must then follow by the employment of the method of monotone sequences. It is also evidently sufficient to suppose all the functions positive.

Let  $E_1, E_2, \dots E_n$  be the  $n$  intervals in which the functions  $f, g$  and  $h$  have respectively the values  $f_1, f_2, \dots f_n, g_1, g_2, \dots g_n$  and  $h_1, h_2, \dots h_n$ .

Then the square of the left-hand side of the inequality to be proved may be written:—

$$(f_1 E_1 + \dots + f_n E_n)^2 + (g_1 E_1 + \dots + g_n E_n)^2 + (h_1 E_1 + \dots + h_n E_n)^2,$$

that is  $\Sigma (f_r^2 + g_r^2 + h_r^2) E_r^2 + 2 \Sigma \Sigma (f_r f_s + g_r g_s + h_r h_s) E_r E_s$ .

The square of the right-hand side of the inequality may be written

$$[\sqrt{(f_1^2 + g_1^2 + h_1^2)} E_1 + \dots + \sqrt{(f_n^2 + g_n^2 + h_n^2)} E_n]^2,$$

that is

$$\Sigma (f_r^2 + g_r^2 + h_r^2) E_r^2 + 2 \Sigma \Sigma \sqrt{(f_r^2 + g_r^2 + h_r^2)} \sqrt{(f_s^2 + g_s^2 + h_s^2)} E_r E_s.$$

Thus the coefficients of  $E_1^2, E_2^2, \dots E_n^2$  on the two sides of the inequality are the same, while the coefficients of  $E_r E_s$  on the left-hand side of the inequality is, by a known theorem in elementary algebra, less than, or equal to, the corresponding coefficient on the right-hand side. Hence the theorem enunciated is true.

*On Change of the Independent Variables in a Multiple Integral.*

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The formula which enables us to transform the independent variables in a multiple integral is well known. It is

$$\int \phi(x) = \int \phi\{x(u)\} \frac{dx}{du} du,$$

where we have for brevity written  $\int$  for the same symbol repeated  $n$  times,  $\phi(x)$  for  $\phi(x_1, x_2, x_3, \dots, x_m)$ ,  $\phi\{x(u)\}$  for the result of substituting in  $\phi(x)$  for the  $x$ 's the functions which they are of the  $n$  variables,  $u_1, u_2, \dots, u_m$ ,  $dx/du$  for the Jacobian of the  $x$ 's with respect to the  $u$ 's,  $dx$  for  $dx_1, dx_2, \dots, dx_m$ , and  $du$  for  $du_1, du_2, \dots, du_m$ , while the field of integration on the right being supposed to be any region or set of points in the flat space defined by the variables  $u$ , that on the left is the corresponding region or set of points in the space defined by the variables  $x$ .

The conditions under which this fundamentally important formula holds have not, however, been stated with any sort of generality, except in the one-dimensional case.

This has been undoubtedly due to the very real difficulties which have been felt in the passage from one dimension to a higher space. Neither the argument employed in the simpler problem, nor the conditions obtained, are generalisable as they stand.

I have recently had occasion to formulate a very general set of conditions under which the formula holds in any number of dimensions, provided only the function  $\phi(x)$  is replaced by unity and the field of integration on the right-hand side is an  $m$ -interval, a term which it is convenient to use for the generalisation in  $m$  dimensions of a rectangular parallelepiped whose faces are parallel to the three co-ordinate planes.

These conditions are, indeed, so general that it scarcely seems possible for them to be improved upon materially.

I propose in my present communication to show how, when once this simpler case has been dealt with, in which  $\phi(x)$  is replaced by unity and the field of integration is restricted to an  $m$ -interval, the more general formula stated at the outset may be deduced. I have purposely so worked the theorem I propose to prove as to make its value independent of the greater or less great generality of the conditions obtained in the simpler problem.

§ 2. The theorem is as follows :—

$$\begin{aligned} \text{If} \quad & x_1 = x_1(u_1, u_2, \dots, u_m), \\ & x_2 = x_2(u_1, u_2, \dots, u_m), \\ & \dots\dots\dots \\ & x_m = x_m(u_1, u_2, \dots, u_m), \end{aligned}$$

define a correspondence between the  $x$ - and the  $u$ -spaces which satisfies the following conditions :—

(1) The functions which the  $x$ 's are of the  $u$ 's are continuous with respect to the *ensemble* of the latter variables.

(2) Every  $m$ -interval in the  $u$ -space has for image a definite portion of the  $x$ -space, whose boundary is the generalisation for such space of the concept of a simple Jordan curve without loops, so that the boundary divides the whole of the  $x$ -space into two distinct portions, one inside and the other outside.

(3) The hypervolume of the portions of  $x$ -space thus enclosed, and which may in particular be evanescent, are given by the absolutely convergent integral

$$\iint \dots \int \frac{d(x_1, x_2, \dots, x_m)}{d(u_1, u_2, \dots, u_m)} du_1, du_2, \dots du_m,$$

taken over the  $m$ -intervals in the  $u$ -space, of which they are the images, the hypervolumes being accordingly positive, negative, or zero, according as the value of this integral is positive, negative, or zero. Then, with the notation explained above, whatever function  $\phi$  may be of the variables  $x$ ,

$$\int \phi(x) dx = \int \phi\{x(u)\} \frac{dx}{du} du,$$

the field of integration on the right being any  $m$ -interval, and that on the left the space  $A$  internal to the boundary which corresponds to the boundary the  $m$ -interval, provided only the function  $\phi$  is summable, not only over this portion of the  $x$ -space, but also over the whole of the set constituted by the points in the  $x$ -space, which are the images of all the points of the  $m$ -interval.

Further, if  $E'$  be any set of points whatever in the  $x$ -space and  $E$  the set of points in the  $u$ -space which has  $E'$  for image, then

$$\int_{E'} \phi(x) dx = \int_E \phi\{x(u)\} \frac{dx}{du} du,$$

provided only the integral on the left exists.

§ 3. The proof of the theorem is the same for any number of dimensions, except as regards notation and terminology. I propose, therefore, for brevity

and simplicity of explanation, to assume henceforth that there are only two independent variables, and I shall call the old variables  $x, y$ , and the new variables  $u, v$ , so that the formula to be proved becomes

$$\iint \phi(x, y) dx dy = \iint \phi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv.$$

The method I adopt, a method I have already had occasion to refer to in previous communications to the Society, is that of monotone sequences. The form in which it is convenient to apply this method on the present occasion is not that in which the theorem to be proved is first discussed for a function  $\phi(x, y)$  which has a finite number of constant values over a finite number of rectangles in the  $(x, y)$ -plane. The convenient plan to employ is now to first prove our theorem, when the function  $\phi(x, y)$  is a continuous function of  $(x, y)$ , and therefore also of  $(u, v)$ , while the field of integration on the right is the rectangle  $a \leq u \leq c, b \leq v \leq d$ .

Divide this rectangle into sub-rectangles by lines drawn parallel to the axes and so near to one another that the image in the  $(x, y)$  plane of every sub-rectangle has a span less than  $\delta$ , where  $\delta$  is itself so small that the oscillation of  $\phi(x, y)$  in each of the little  $(x, y)$  area-images is less than  $\epsilon$ . This is possible owing to the continuity of the correspondence and the continuity of the function  $\phi$ , by virtue of the well-known theorem that continuity involves uniform continuity.

We may, evidently without loss of generality, assume that the area  $A$  in the  $(x, y)$ -plane corresponding to the fundamental rectangle in the  $(u, v)$ -plane is positive. We may also suppose the function  $\phi$  to be never negative, for, if not, it could be expressed as the difference of two functions each of which is continuous and neither of which is negative.

Let us agree to denote by the same letter the name and the area of each portion of either plane considered. Let  $\Delta$  be the typical little rectangle in the  $(u, v)$ -plane and  $\Delta'$  its image in the  $(x, y)$ -plane. Then the areas  $\Delta$  are all positive, but the areas  $\Delta'$  are in general some positive and some negative. The areas  $\Delta$  add up as they stand to the fundamental rectangle. The areas  $\Delta'$  overlap and have for their algebraical sum the area  $A$ . Also, as the boundary of each  $\Delta'$  divides the plane into two distinct parts, they cut one another up into a finite number of non-overlapping areas  $\Delta''$ , each of which will necessarily occur an odd number of times,  $2p+1$ , say,  $p+1$  times positively and  $p$  times negatively, whenever  $\Delta''$  is inside  $A$ , where  $p$  varies, of course, in general from one  $\Delta''$  to another. Such  $\Delta''$ , however, as are outside  $A$  will each occur an even number of times, say  $2p$ ,  $p$  times positively and  $p$  times negatively.

We are thus finally left with a set of essentially positive  $\Delta''$ 's, of which each occurs only once inside and does not occur at all outside  $\Lambda$ , their sum being exactly equal to  $\Lambda$ . Moreover, as every  $\Delta''$  is contained in a  $\Delta'$ , the oscillation of  $\phi(x, y)$  in every  $\Delta''$  is less than  $\epsilon$ . Hence, by the definition of a double integral of a continuous function

$$\iint \phi(x, y) dx dy,$$

taken over the area  $\Lambda$ , differs from the sum of the products of each  $\Delta''$  into the value,  $q$  say, of  $\phi(x, y)$  at any convenient point in it ( $q$  varying, of course, in general from one  $\Delta''$  to another) by a quantity which is less than the product of  $\epsilon$  into the sum of the  $\Delta''$ 's, that is by less than  $\epsilon\Lambda$ .

All turns now on expressing this summation involving  $\Delta''$  in terms of two summations involving  $\Delta'$ , which we shall call respectively the upper and lower  $\Delta'$ -summations. By the upper  $\Delta'$ -summation we shall mean that obtained by summing the products of each  $\Delta'$  into a value of  $\phi$ , chosen to be the upper bound of  $\phi$  in that  $\Delta'$ , when  $\Delta'$  is positive, and the lower bound, when  $\Delta'$  is negative. By the lower  $\Delta'$ -summation we shall understand that obtained from the upper summation when the words upper bound and lower bound are interchanged. Then we assert that—

(1) The  $\Delta''$ -summation has a value intermediate between those of the upper and lower  $\Delta'$ -summations.

(2) The value of the upper  $\Delta'$ -summation exceeds that of the lower by a quantity which is less than the product of  $\epsilon$  into the sum of the  $\Delta''$ 's, each taken positively.

To prove (1), we remark that  $\Delta''$  will virtually occur in  $2p+1$  terms of the  $\Delta'$  upper summation, as being part of  $2p+1$   $\Delta''$ 's, and will accordingly contribute to the  $\Delta'$  upper summation in all

$$\Delta'' (U_1 + U_2 + \dots + U_{p+1} - L_1 - L_2 \dots - L_p),$$

where  $U_1, U_2, \dots, U_{p+1}$ , are the upper bounds of  $\phi$  in the  $p+1$  positive  $\Delta''$ 's which contain  $\Delta''$ , and  $L_1, L_2, \dots, L_p$  are the lower bounds of  $\phi$  in the  $p$  negative  $\Delta''$ 's which contain  $\Delta''$ . Each of the  $U$ 's is  $\geq q$ , and each of the  $L$ 's is  $\leq q$ . Hence the contribution of  $\Delta''$  is greater or equal to

$$\Delta'' [(p+1)q - p \cdot q],$$

that is, greater or equal to

$$q \cdot \Delta''.$$

Hence, the portion of the  $\Delta'$  upper summation due to such a  $\Delta''$  is greater or equal to the corresponding part of the  $\Delta''$ -summation.

We have also to consider the  $\Delta''$ 's which occur the same number of times



positively and negatively outside  $A$ . Here the  $U$ 's of the positive  $\Delta$ 's, being greater or equal to any value of  $\phi$  chosen in  $\Delta''$ , are greater or equal to the  $L$ 's in the negative  $\Delta$ 's. Hence, though the  $U$ 's are now equal to the  $L$ 's in number, the excess of the sum of the former of that of the latter is necessarily positive, so that the portion of the  $\Delta'$  upper summation due to the parts of the  $\Delta$ 's outside  $\Delta$  is certainly positive, while there is no corresponding portion in the  $\Delta''$ -summation.

It at once follows that the  $\Delta''$ -summation is not greater than the  $\Delta'$  upper summation. Similarly, it is not less than the  $\Delta'$  lower summation. Hence our assertion (1) is true.

As regards our assertion (2), it is sufficient to remark that it is an immediate consequence of our mode of forming the summations, coupled with the uniformity of the continuity of  $\phi$ .

It follows, since the area  $\Delta'$  is numerically equal to

$$\left| \iint \frac{d(x, y)}{d(u, v)} du dv \right|$$

taken over  $\Delta$ , and therefore numerically

$$= \iint \left| \frac{d(x, y)}{d(u, v)} \right| du dv,$$

taken over  $\Delta$ , that the  $\Delta''$  and  $\Delta'$ -summations all differ from one another by a quantity which is numerically less than

$$e \iint \left| \frac{d(x, y)}{d(u, v)} \right| du dv,$$

taken over the area  $A$ .

But the  $\Delta''$ -summation has been shown to differ from

$$\iint \phi(x, y) dx dy \tag{1}$$

taken over  $A$  by less than  $eA$ . Hence  $\iint \phi(x, y) dx dy$  must differ from either of the  $\Delta'$ -summations by a quantity which is numerically less than

$$eA + e \iint \left| \frac{d(x, y)}{d(u, v)} \right| du dv, \tag{2}$$

where the integral is taken over  $A$ .

Now take either, say the upper, of the  $\Delta'$ -summations. It may be written in the form

$$\Sigma \Sigma \phi(x', y') \iint \frac{d(x, y)}{d(u, v)} du dv, \tag{3}$$

where the integral is taken over  $\Delta'$ , and  $x', y'$  is the point of  $\Delta'$  at which  $\phi$  assumes its upper bound in  $\Delta'$ . This summation differs therefore from

$$\iint \phi \{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv \tag{4}$$

by 
$$\iint \{ \phi [x(u, v), y(u, v)] - \phi [x'(u, v), y'(u, v)] \} \frac{d(x, y)}{d(u, v)} du dv$$

taken over the whole area  $A$ ,  $x', y'$  changing of course by jumps as we move from one  $\Delta$  of the fundamental rectangle to another.

Now the coefficient of  $d(x, y)/d(u, v)$  in the integrant being numerically less than  $\epsilon$ , it follows at once that the difference between the double summation (3) and the double integral (4) is numerically less than

$$\epsilon \iint \left| \frac{d(x, y)}{d(u, v)} \right| du dv.$$

Hence the double integral (1) differs from the double integral (4) by less than the sum of the last expression and (2). That is by less than

$$\epsilon A + 2\epsilon \iint \left| \frac{d(x, y)}{d(u, v)} \right| du dv.$$

Hence, as  $\epsilon$  is at our disposal, (1) and (4) must be equal.

§ 4. Next let  $\phi(x, y)$  denote any bounded function obtainable from the continuous function  $\phi(x, y)$  by monotone sequences, in other words, any bounded lower or upper semi-continuous function, or any  $lu, ul \dots$  function. The truth of our theorem in this case follows immediately. In fact, if, for example,  $\phi_1(x, y), \phi_2(x, y), \dots, \phi_n(x, y)$  represent any monotone sequence of functions for each of which the theorem has been proved to be true, while the limit  $\phi$  of the sequence is a bounded function, then the integral of  $\phi$  over the area  $A$  is the limit of that of  $\phi_n$ . Moreover, the monotone sequence of functions of  $u, v$ , of which the typical member is  $\phi_n \{x(u, v), y(u, v)\}$ , may, by a known theorem, be integrated term-by-term after being multiplied by the summable function  $d(x, y)/d(u, v)$ . Whence it follows that, since the theorem holds for every  $\phi_n$ , it holds for  $\phi$ . Thus the theorem holds for every bounded function defined by sequences, or, as we may say, definable mathematically, the field of integration on the right being the fundamental rectangle, and that on the left the area  $A$ .

§ 5. We shall now find it convenient to prove the following theorem:—

**THEOREM.**—If the conditions of § 1 and § 2 for the correspondence between the  $(x, y)$  and the  $(u, v)$ -planes hold, then every set of zero content in the  $(x, y)$ -plane is either the image of a set of zero content in the  $(u, v)$ -plane or the set of positive content of which it is the image, is such that  $d(x, y)/d(u, v)$  is zero at all points of this set of positive content except those belonging to, at most, a set of zero content.

**PROOF.**—Every set of positive content is the sum of a set of zero content and of an outer limiting set, or as we call it an  $O$ -set. It is therefore clearly sufficient to prove that if a set of zero content in the  $(x, y)$  area is the image

of an  $O$ -set in the  $(u, v)$  rectangle, then  $d(x, y)/d(u, v) = 0$  "almost everywhere" in this  $O$ -set. Let  $Q$  be the subset of this  $O$ -set at which  $d(x, y)/d(u, v) \geq 0$ , and let  $Q'$  be the image of  $Q$ , so that  $Q'$  has zero content. Then the function which is unity at every point of  $Q'$  and zero elsewhere, and the function which is unity at every point of  $Q$  and zero elsewhere, are both necessarily obtainable by monotone sequences. Writing for  $\phi(x, y)$  in § 4 the former function, and therefore for  $\phi\{x(u, v), y(u, v)\}$ , the latter function, we obtain then

$$0 = \iint_{Q'} dx dy = \iint_Q \frac{d(x, y)}{d(u, v)} du dv.$$

Hence the Jacobian must vanish "almost everywhere" in  $Q$ ; in other words, in that part of the  $O$ -set at which the Jacobian is known to be not negative. Similarly, it vanishes "almost everywhere" in that part at which it is negative. Hence it vanishes "almost everywhere" in the  $O$ -set, as was to be proved.

§ 6. Now let  $\phi$  be any bounded function possessing a Lebesgue integral. Then we know that it can be enclosed between a  $u$ l function  $\phi_1$  and a  $u$ l function  $\phi_2$  having the same integral. Also, by § 4, we know

$$\begin{aligned} \iint \phi_1(x, y) dx dy &= \iint \phi_1\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv, \\ \iint \phi_2(x, y) dx dy &= \iint \phi_2\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv, \end{aligned}$$

where by definition

$$\iint \phi(x, y) dx dy = \iint \phi_1(x, y) dx dy = \iint \phi_2(x, y) dx dy.$$

Now  $\phi_1(x, y)$  differs from  $\phi_2(x, y)$  only as a set of content zero in the  $(x, y)$ -plane, and therefore, by the theorem just proved,  $\phi_1\{x(u, v), y(u, v)\}$  and  $\phi_2\{x(u, v), y(u, v)\}$  either agree for all values of  $u$  and  $v$  except such as belong to a set of content zero of the  $(u, v)$ -plane, or, if they differ at other points,  $d(x, y)/d(u, v)$ , is there zero. Thus we shall make no mistake if, in integrating with respect to  $(u, v)$ , we write  $\phi_1 = \phi_2 = \phi$ . In other words, we have

$$\iint \phi(x, y) dx dy = \iint \phi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv,$$

whatever bounded function  $\phi$  may be.

§ 7. Now let  $\phi$  denote any unbounded summable function supposed, as may be done without loss of generality, to be positive; let  $\phi_n$  be the function which is equal to  $\phi$  wherever  $\phi \leq n$ , and have the value  $n$  elsewhere, so that

$$\phi_n \leq \phi_{n+1} \leq \dots \rightarrow \phi.$$

Then it is evident that, by the preceding section, as  $\phi_n$  is bounded, we may write  $\phi_n$  for  $\phi$  in the equation at the end of that section. Moreover, by definition

$$\iint \phi_n(x, y) dx dy \rightarrow \iint \phi(x, y) dx dy.$$

Hence 
$$\lim_{n \rightarrow \infty} \iint \phi_n \{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv = \iint \phi(x, y) dx dy.$$

If now  $d(x, y)/d(u, v)$  never changes sign, so that without loss of generality we may suppose it to be positive, the integrant of the integral on the left-hand side traces out a monotone increasing sequence, accordingly we may introduce the limit inside the integral, so that if  $\phi_n$  nowhere assumes an infinite value, the required result at once follows. If, on the other hand,  $\phi(x, y)$  assumes infinite values, we cannot go further unless we make the convention that  $\phi\{x(u, v), y(u, v)\}d(x, y)/d(u, v)$  is to be regarded as having the value zero whenever  $d(x, y)/d(u, v)$  is zero. With this convention, the result again follows by virtue of the theorem proved in § 5.

§ 8. If, however,  $d(x, y)/d(u, v)$  does not preserve the same sign throughout the fundamental rectangle, the above argument fails. In order to understand the reasoning required in this latter case, we have to bear carefully in mind the sense in which we have used the word image. The point which corresponds to an assigned point of the fundamental rectangle in the correspondence is not necessarily a point of the image  $A$  of the fundamental rectangle, but may be outside  $A$ , though in the aggregate such points, as will be seen by referring to § 3, belong to areas  $\Delta'$  which cross one another out, so that the points themselves may be said, in a certain sense, to cross one another out also. The reasoning employed in that section shows that we require to assume that  $\phi$  exists and possesses the properties ascribed to it, not only over the image  $A$  of the fundamental rectangle, but over all that portion of the  $(x, y)$  plane outside  $A$  constituted by the points which correspond to points of the fundamental rectangle without being included in  $A$ . It is the recognition of this tacitly assumed existence of  $\phi$  outside  $A$  which enables us to complete our reasoning. The value, in fact, of  $\phi\{x(u, v), y(u, v)\}$  at a point  $(u, v)$  of the fundamental rectangle which has for image a point  $(x, y)$  outside  $A$ , is necessarily the values of  $\phi(x, y)$  at this latter point.

Let us then now define a new function  $\psi(x, y)$  equal to  $\phi(x, y)$  at all the points, both inside and outside  $A$ , which correspond to the points inside the fundamental rectangle where  $d(x, y)/d(u, v)$  is positive, and equal to  $\phi(x, y)$  with its sign changed at all the points, both inside and outside  $A$ , which correspond to points of the fundamental rectangle where  $d(x, y)/d(u, v)$  is negative.

## 90 *Change of the Independent Variables in a Multiple Integral.*

Then it is evident that (1), as  $\phi(x, y)$  is summable not only inside but outside  $A$ , so is  $\psi(x, y)$ ; (2),  $\psi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)}$  is everywhere positive throughout the whole of the fundamental rectangle. Also let  $\psi_n(x, y)$  be a function which is defined to be equal to  $\psi(x, y)$  wherever  $|\psi(x, y)| \leq n$ , and let  $\psi_n(x, y)$  be equal to  $n$ , where  $\psi(x, y)$  is positive and greater than  $n$ , and be equal to  $-n$ , wherever  $\psi(x, y)$  is negative and less than  $-n$ . Then, since  $\psi_n(x, y)$  is bounded, it follows by means of § 6, in the same manner as in § 7, that

$$\lim_{n \rightarrow \infty} \iint \psi_n\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv = \iint_A \psi(x, y) dx dy.$$

Also the integrant of the integral on the left is clearly positive.

Hence, a reasoning precisely analogous to that of the latter part of § 7 shows that

$$\iint \psi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv = \iint_A \psi(x, y) dx dy.$$

Thus the integral on the left-hand side, taken over the whole of the fundamental rectangle, necessarily exists. But  $\phi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)}$  is everywhere numerically equal to the positive function  $\psi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)}$ , and is accordingly summable over the fundamental rectangle. Hence  $\phi_n\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)}$  is necessarily numerically less than this latter function, that is, the succession of which it is the typical term has every one of its terms numerically less than one and the same summable function of  $(u, v)$ . Hence, by the theory of integration of sequences, we may integrate it term by term, and write

$$\begin{aligned} \lim_{n \rightarrow \infty} \iint \phi_n\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv \\ = \iint \lim_{n \rightarrow \infty} \phi_n\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv, \end{aligned}$$

and accordingly, with the same convention as that explained in § 7,

$$= \iint \phi\{x(u, v), y(u, v)\} \frac{d(x, y)}{d(u, v)} du dv.$$

This last expression is accordingly equal to  $\iint \phi(x, y) dx dy$ .

It remains only to replace the area  $A$ , which is the field of integration of this latter integral, by any set of points,  $E'$ , in that area, and the fundamental rectangle of the  $(u, v)$ -plane by the set  $E$ , of which  $E'$  is the image. To show that this is possible, it suffices to remark that we may replace

$\phi(x, y)$  by a new function defined as the product of  $\phi(x, y)$  into that function of  $(x, y)$  which has the value unity at all points of  $E'$  and is zero elsewhere, and, accordingly,  $\phi\{x(u, v), y(u, v)\}$ , by the product of this function into a function of  $(u, v)$ , which is defined to have the value unity at all points of the set  $E$  which has  $E'$  for image and is zero elsewhere. We then at once have the desired result, except that there remains a doubt as to the type of summability required for  $\phi(x, y)$ . This must be such that, when multiplied by the auxiliary function just introduced, it is summable over the whole set of points which corresponds to the fundamental rectangle. But this is clearly the same as demanding that  $\phi(x, y)$  should be summable over the set of points constituted by all the points in the  $(x, y)$ -plane which correspond to the set  $E$ , that is, over the set  $E'$ .

Hence our theorem has been proved, with all the generality given to it, in the enunciation of § 2.

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*On Certain Independent Factors in Mental Measurements.*

By J. C. MAXWELL GARNETT (late Fellow of Trinity College, Cambridge).

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I.

In a paper published in the 'American Journal of Psychology' for 1904, Prof. Spearman argued that "all branches of intellectual activity have in common one fundamental function (or group of functions),"\* and even that this fundamental function enters into sensory discrimination no less truly than into more complicated intellectual activities. In 1909 Mr. Cyril Burt described† experiments on two groups of Oxford schoolboys undertaken "with a view to testing in practice the mathematical methods of Prof. Spearman." Mr. Burt calculated the correlations between the performances of his subjects in 12 different tests, which he classified as sensory, motor, sensori-motor, and association tests, together with one (the twelfth) test of voluntary attention. Mr. Burt's results were consistent with the view that all the correlations were due to the operation of one and only one general factor. Two years later Prof. Spearman and Dr. Hart‡ proposed a new test

\* 'American Journal of Psychology,' vol. 15, p. 284 (1904).

† 'British Journal of Psychology,' vol. 3, pp. 94-177 (1909-10).

‡ 'British Journal of Psychology,' vol. 5, p. 51 (1912-13).

for a (single) general factor; namely that, in such a correlation table as those published by Mr. Burt, in the form (27) below, the correlation between every pair of columns should, with proper allowance for sampling errors, be +1, or, as Dr. Webb\* pointed out afterwards, -1. Their formula for column correlation, corrected for errors of sampling, is

$$R_{ab}' = \frac{S(\rho_{xa}\rho_{xb}) - (n-1)\overline{r_{ab}}\overline{\sigma_{xa}\sigma_{xb}}}{\sqrt{[S(\rho_{xa}^2) - (n-1)\overline{\sigma_{xa}^2}]}\sqrt{[S(\rho_{ab}^2) - (n-1)\overline{\sigma_{xb}^2}]}}$$

in which the  $\rho$ 's are the correlation coefficients  $r$  measured from the mean of the column, and the  $\sigma$ 's are the probable errors of the  $r$ 's divided by 0.6745. The bar indicates mean values. The authors decided that, for the purpose of calculating a "correlation between columns," only those pairs of columns could be used in which  $S(\rho^2)$  is at least twice the correction  $(n-1)\sigma^2$ . With this limitation, they applied their formula to the five largest pairs and the five smallest pairs (or as many as were up to the correctional standard) of columns in 14 published tables of correlation coefficients dating from various periods up to 30 years back. They found that "from beginning to end, the correlation between columns is positive and very high; the mean is almost complete +1. This is just the value demanded by the theory of a [single] General Factor."† Dr. Webb, in his essay on "Character and Intelligence," to which reference has just been made, prepared a further correlation table of five columns (and five rows) the results of five examination tests set to 96 training college students. Nine out of the ten pairs of columns were up to the correctional standard of Prof. Spearman and Dr. Hart, and the application of their formula to those nine pairs yielded  $1.02 \pm 0.08$  as the average correlation between columns. This result, says Dr. Webb, "is an additional item of evidence in support of the theory of a general factor. . . . It takes its place in the huge array of evidence collected by Prof. Spearman from experimental tests by many investigators—the steadiness of results being such as to rival the niceties which physical measurements reveal. It should be remembered that the raw material for our own (comparatively small) contribution to this result consisted of test-papers numbering nearly 10,000."‡

Prof. Spearman's mathematical argument for the existence of general ability has, however, been challenged. Thus Mr. Thomson concludes a recent paper§ on the subject with the words: "It must not hastily and illogically be concluded by any one that general ability is a fiction. Its existence or non-

\* "Character and Intelligence" (B.J.P. Monograph Supplement, 1915).

† *Loc. cit.*, p. 60.

‡ *Loc. cit.*, p. 37.

§ 'British Journal of Psychology,' vol. 3, p. 271 (1909-10).

existence is, as far as the mathematical argument goes, an entirely open question."\*

It is with the mathematical argument that the present paper is principally concerned. We shall consider what consequences necessarily follow when the correlation between every pair of columns in a correlation table is  $\pm 1$ ; and we shall find that the correlation between every pair of columns will only be  $\pm 1$  if there is one, and only one, general factor,† either of the correlated variables themselves (if Mr. Burt's conditions—equations (24), below—for a hierarchy are satisfied), or of the differences between these variables and a real multiple of a new variable that is independent of them all.

## II.

Let us suppose that the mental qualities measured in any particular investigation are due to a number  $n$  of independent factors  $X_1, X_2, \dots X_n$ . Let  $x_1, x_2, \dots x_n$  measure the amounts of these factors (or qualities) possessed in excess of the average by any subject (person investigated). We shall assume that, among a very large number of subjects, each quality is distributed according to the normal law; so that the probability that any particular subject will possess a factor—say  $X_p$ —in a degree lying between  $x_p$  and  $x_p + \delta x_p$  is  $\frac{1}{\sqrt{(2\pi)\sigma_p}} e^{-\frac{1}{2}x_p^2/\sigma_p^2} \delta x_p$ . Let us now choose our units of measurement for  $X_1 \dots X_n$  so that  $\sigma_1 = \sigma_2 = \dots = \sigma_n \equiv \sigma$ . Some arbitrary choice has to be made; how else are we to represent, say, "degree of sense of humour" by a number?‡ We, therefore, choose our units for measuring the  $n$  independent factors so that the standard deviations of the normal distributions of each factor shall be equal to  $\sigma$ .

\* *Loc. cit.*, p. 280.

† [Note added, March 24, 1919.—More precisely expressed, our result will be that whenever the correlation between  $n$  variables (as, for example, the measures of  $n$  mental qualities), each of which is distributed according to the normal law with the same probable error, satisfy the "correlation between columns" condition, these  $n$  variables (or, if their correlations do not satisfy Mr. Burt's conditions for a hierarchy, the  $n$  differences between them respectively and a real multiple of an  $(n+1)$ th variable, independent of them all, but distributed according to the normal law, with still the same probable error), can be completely expressed as linear functions of  $n+1$  independent variables, each of which is distributed according to the normal law with the same probable error, and one of which is a *single general factor*, while the remainder are *specific factors*.]

‡ Dr. Webb, in his investigation of mental qualities, adopted such units for the measurement of each quality as would give the same constant (standard deviation) to the frequency distribution of each of the forty-eight qualities with which he was concerned (*loc. cit.*, pp. 18, 19; see especially the footnote on these two pages).





This result may also be obtained by noticing that any individual possessing the  $n$  independent factors  $X_1, X_2, \dots, X_n$ , in degrees  $x_1, x_2, \dots, x_n$ , may be represented in  $n$ -dimensional space by a point whose co-ordinates are  $x_1, x_2, \dots, x_n$ ; and that, when the number of individuals is very large, the density of distribution of such points, being given by equation (2), is a function only of the distance  $(x_1^2 + x_2^2 + \dots + x_n^2)^{\frac{1}{2}}$  from the origin, so that the density of distribution of the points representing individuals falls off according to the normal law (with the same standard deviation) in whatever direction— $Ox_1, Ox_2, \dots, Ox_n$ , or  $Oq$ —we proceed straight out from the origin.

No distribution of the quality  $Q$ , except such as is defined by a linear equation of the type (8), will satisfy the relation (9). For consider variations of two independent variables at a time. The probability that a subject chosen at random will possess these qualities ( $X_1$  and  $X_2$ , say) in degrees intermediate between  $x_1$  and  $x_1 + \delta x_1$  and  $x_2$  and  $x_2 + \delta x_2$  respectively, is

$$Ae^{-(x_1^2 + x_2^2)/2\sigma^2} \delta x_1 \delta x_2$$

where  $A$  is independent of  $x_1$  and  $x_2$ . We may represent this distribution by a surface of revolution about an axis,  $Oz$ , perpendicular to  $Ox_1$  and  $Ox_2$ . Every section of this surface by a plane perpendicular to that of  $Ox_1$  and  $Ox_2$  is a normal probability curve. For example, the section of

$$z = Be^{-(x_1^2 + x_2^2)/2\sigma^2} \quad (10)$$

by such a plane passing through the point  $x_1, x_2$  and the origin has the equation

$$z = Be^{-y^2/2\sigma^2}, \quad (11)$$

while the section through the same point, but parallel to  $zOx_1$ , has the equation  $z = Ce^{-y^2/2\sigma^2}$  where the constant  $C$  is given by  $C = Be^{-x_2^2/2\sigma^2}$ . Similarly, sections by other planes perpendicular to  $x_1Ox_2$ , but having different traces on  $x_1Ox_2$ , would be probability curves with still other constants. It follows that a section of the surface given by equation (10) by a surface generated by lines parallel to  $Oz$  but intersecting  $x_1Ox_2$  in any curve  $F(x_1, x_2) = 0$  which is not a straight line, would not be a normal curve. We conclude that every quality  $Q$  that is distributed according to the normal curve must be related to the independent variables (factors) by a linear relation as in equation (8).

For example, if "degree of sense of humour" be distributed normally and depend on two and only two independent factors, say "ability" and "cleverness," both normally distributed, then "sense of humour" must be the sum of (equal or different) proportions of the two factors, but cannot be their product, quotient, or any other function of them.

Consider now the Bravais-Pearson correlation  $r_{qq'}$  between  $Q$  and some other quality  $Q'$  measured by

$$q' = l_1'x_1 + l_2'x_2 + \dots + l_n'x_n \quad (12)$$

$$\text{where, as before,} \quad l_1'^2 + l_2'^2 + \dots + l_n'^2 = 1. \quad (13)$$

It will be convenient to write

$$e^2 = x_1^2 + x_2^2 + \dots + x_n^2 \quad (14)$$

so that  $e$  is a measure of the extent to which a subject is exceptional, regard being had to all the variables involved. Then our result (2) above may be re-written

$$\frac{1}{(2\pi\sigma^2)^{n/2}} e^{-e^2/2\sigma^2} \delta x_1 \delta x_2 \dots \delta x_n = d \cdot \delta x_1 \dots \delta x_n, \text{ say} \quad (15)$$

giving the probability that a subject will possess the various qualities in degrees lying between  $x_1$  and  $x_1 + \delta x_1$ , etc. Here  $d$  is a measure of the density of distribution of subjects.

According to the definition of  $r_{qq'}$ , we have

$$\begin{aligned} r_{qq'} &= \frac{\iint \dots [d \cdot qq' dx_1 dx_2 \dots dx_n]}{\sqrt{(\iint \dots [d \cdot q^2 dx_1 dx_2 \dots dx_n])} \sqrt{(\iint \dots [d \cdot q'^2 dx_1 dx_2 \dots dx_n])}} \\ &= \frac{\iint \dots [e^{-(x_1^2 + x_2^2 + \dots + x_n^2)/2\sigma^2} (l_1 x_1 + \dots + l_n x_n) (l_1' x_1 + \dots + l_n' x_n) dx_1 \dots dx_n]}{\sqrt{[\iint \dots [e^{-(x_1^2 + \dots + x_n^2)/2\sigma^2} (l_1 x_1 + \dots + l_n x_n)^2 dx_1 \dots dx_n]]} \cdot \sqrt{[\iint \dots [e^{-(x_1^2 + \dots + x_n^2)/2\sigma^2} (l_1' x_1 + \dots + l_n' x_n)^2 dx_1 \dots dx_n]]}} \\ &= \frac{l_1 l_1' + l_2 l_2' + \dots + l_n l_n'}{\sqrt{(l_1^2 + l_2^2 + \dots + l_n^2)} \sqrt{(l_1'^2 + l_2'^2 + \dots + l_n'^2)}} \end{aligned}$$

on dividing numerator and denominator by  $\int_{-\infty}^{\infty} e^{-x^2/2\sigma^2} x^2 dx$ .

Hence\* the "cosine law,"

$$r_{qq'} = l_1 l_1' + l_2 l_2' + \dots + l_n l_n'. \quad (16)$$

We note that, if there are only three independent factors and if we measure  $x_1, x_2, x_3$  along three axes at right angles,  $l_1, l_2, l_3$ , etc., become direction-cosines, so that  $q$  is measured in the direction  $l_1, l_2, l_3$ , or, say,  $Oq$ . Then the last equation becomes

$$r_{qq'} = \cos qOq' \quad (17)$$

affording us a very simple geometrical conception of the measure of correlation.

Moreover, however large may be the number  $n$  of independent variables,

\* [Note added, March 24, 1919.—A result equivalent to that given in equation (16) was obtained by Bravais in 1848: see "Analyses Mathématiques sur les Probabilités des Erreurs de Situation d'un Point," "Mémoires de l'Institut de France," IX, pp. 260 et seq.]

we can, by a linear transformation of the type shown in equations (3) to (7), choose new independent variables, such that  $Q$  and  $Q'$  depend on two, and two only, among them; so that equation (17) still holds when the number of independent variables exceeds three. This equation may be interpreted to mean that  $r_{qq'}$  represents the average deviation in  $q$  (or  $q'$ ) corresponding to unit deviation in  $q'$  (or  $q$ ).

The condition that, with only three independent variables, three qualities,  $Q_1$ ,  $Q_2$ , and  $Q_3$ , should be dependent on two, and two only, follows at once. The condition in question is that  $Oq_1$ ,  $Oq_2$ , and  $Oq_3$  should lie in a plane, or that

$$q_2 \hat{O} q_3 + q_3 \hat{O} q_1 + q_1 \hat{O} q_2 = 0,$$

or that\*  $\cos^{-1} r_{23} + \cos^{-1} r_{31} + \cos^{-1} r_{12} = 0. \quad (18)$

It is easy to show that, however many independent variables ( $x_1, x_2, \dots, x_n$ ) there may be, equation (18) still gives the condition that three qualities,  $Q_1$ ,  $Q_2$ , and  $Q_3$ , should contain two, and only two, independent general factors, and that no one of them should contain any specific factor in addition.†

If in equation (16) we make  $Q'$  identical with  $X_1, \dots, X_n$ , in turn we obtain the correlations between  $Q$  and the independent variables. They are

$$r_{qx_1} = l_1; \quad r_{qx_2} = l_2; \quad \dots; \quad r_{qx_n} = l_n. \quad (19)$$

Again, let us take  $Q'$  so as to be independent of  $X_1$  (*i.e.*  $l'_1 = 0$ ), but so as to

\* [Note added March 24, 1919.—This equation (18) may be written

$$r_{23}^2 + r_{31}^2 + r_{12}^2 - 2r_{23}r_{31}r_{12} = 1 \dots \quad (18')$$

It may be shown, by employing the formulæ of spherical trigonometry, that the corresponding condition that four qualities  $Q_1, Q_2, Q_3$ , and  $Q_4$ , should depend on three independent factors only (or, in other words, that  $Oq_1, Oq_2, Oq_3$ , and  $Oq_4$ , should lie in the same 3-dimensional space) is, if

$$\begin{aligned} r_{12} = \alpha, \quad r_{13} = \beta, \quad r_{14} = \gamma, \quad r_{23} = \delta, \quad r_{24} = \epsilon, \quad r_{34} = \zeta, \\ \alpha^2 + \beta^2 + \gamma^2 + \delta^2 + \epsilon^2 + \zeta^2 - 2(\beta\gamma\zeta + \alpha\gamma\epsilon + \alpha\beta\delta + \delta\epsilon\zeta) - (\alpha^2\zeta^2 + \beta^2\epsilon^2 + \gamma^2\delta^2) \\ + 2(\beta\gamma \cdot \delta\epsilon + \gamma\alpha \cdot \delta\zeta + \alpha\beta \cdot \zeta\epsilon) = 1 \dots \quad (18'') \end{aligned}$$

† If three qualities,  $Q_1, Q_2, Q_3$ , contain two, and only two, independent general factors  $X$  and  $Y$ , and no specific factors, we may write

$$\begin{aligned} q_1 &= l_1x + m_1y = x \cos \theta_1 + y \sin \theta_1, \\ q_2 &= l_2x + m_2y = x \cos \theta_2 + y \sin \theta_2, \\ q_3 &= l_3x + m_3y = x \cos \theta_3 + y \sin \theta_3, \end{aligned}$$

so that equation (16) gives

$$r_{12} = l_1l_2 + m_1m_2 = \cos(\theta_1 - \theta_2).$$

Since, therefore,

$$(\theta_2 - \theta_3) + (\theta_3 - \theta_1) + (\theta_1 - \theta_2) = 0,$$

we have

$$\cos^{-1} r_{23} + \cos^{-1} r_{31} + \cos^{-1} r_{12} = 0.$$

contain  $X_2, \dots, X_n$  in the same proportions as these  $n-1$  variables are contained in  $Q$ . Then we have

$$l_1' = 0; \quad \frac{l_2'}{l_2} = \frac{l_3'}{l_3} = \dots = \frac{l_n'}{l_n} = \frac{\sqrt{(l_2'^2 + \dots + l_n'^2)}}{\sqrt{(l_2^2 + \dots + l_n^2)}} = \frac{1}{\sqrt{(1-l_1^2)}}$$

in view of equation (7). If, now, we have some other quality  $P(k_1, \dots k_n)$  related to  $P'(k'_1, \dots k'_n)$  as  $Q$  is related to  $Q'$ , we have

$$\begin{aligned} r_{PQ}(x, \text{constant}) &\equiv r_{P'Q'} = k_1' l_1' + k_2' l_2' + \dots + k_n' l_n' \\ &= \frac{k_2 l_2 + k_3 l_3 + \dots + k_n l_n}{\sqrt{(1-k_1^2)} \sqrt{(1-l_1^2)}} \\ &= \frac{r_{PQ} - k_1 l_1}{\sqrt{(1-k_1^2)} \sqrt{(1-l_1^2)}} \end{aligned} \quad (20)$$

which is Yule's well-known equation.

One other result we may note in passing. In dice-throwing experiments the score of each die is an independent variable. If  $q$  represent the total score obtained by throwing  $n$  dice multiplied by a factor that will give to  $q$  the same mean variation\* as  $x_1, x_2, \dots$ , or  $x_n$ , the scores obtained by the separate dice, we have

$$q = l_1 x_1 + l_2 x_2 + \dots + l_n x_n$$

where 
$$l_1 = l_2 = \dots = l_n = \sqrt{\frac{(l_1^2 + l_2^2 + \dots + l_n^2)}{n}} = \frac{1}{\sqrt{(n)}}$$

so that 
$$q = \frac{1}{\sqrt{(n)}} (x_1 + x_2 + \dots + x_n). \quad (21)$$

We note that the correlations of any  $q$  distribution are the same as those of the scores  $(x_1 + x_2 + \dots + x_n)$ , to which the  $q$ 's bear a constant proportion  $1/\sqrt{(n)}$ . If, as in Mr. Thomson's† experiment, we wish to know the correlation between a large number of successive pairs of throws of dice, such that  $l+m$  dice are thrown for the first throw,  $l$ , left lying, and  $k$  thrown to form with  $l$  the second throw of  $l+k$  dice, and, if  $S$  and  $S'$  be successive scores, we have

$$\left. \begin{aligned} S &= x_1 + x_2 + \dots + x_l + x_{l+1} + \dots + x_{l+m} = q \sqrt{(l+m)} \\ S' &= x_1 + x_2 + \dots + x_l + x_{l+1}' + \dots + x_{l+k}' = q' \sqrt{(l+k)} \end{aligned} \right\} \quad (22)$$

\* The amount of this mean variation,  $\sigma$ , is easily determined. If each die possesses  $2a+1$  faces marked  $-\alpha, -\alpha-1, \dots -1, 0, 1, \dots \alpha-1, \alpha$  then, in a very large number of throws, say  $N(2a+1)$ , each face will turn up  $N$  times, so that

$$N(2a+1)\sigma^2 = 2N(1^2 + 2^2 + \dots + a^2) = \frac{N}{3} a(a+1)(2a+1),$$

giving

$$\sigma^2 = \frac{1}{3} a(a+1).$$

† 'British Journal of Psychology,' vol. 8, p. 274 (1916).

where  $x_{l+1}', x_{l+2}', \dots, x_{l+k}'$  are variables independent of  $x_{l+1}, \dots, x_{l+m}$  so that equation (16) gives

$$r_{ss'} = r_{qq'} = \frac{1}{\sqrt{(l+m)}} \cdot \frac{1}{\sqrt{(l+k)}} + \dots + \frac{1}{\sqrt{(l+m)}} \cdot \frac{1}{\sqrt{(l+k)}} \quad (l \text{ terms})$$

$$= \frac{l}{\sqrt{(l+m)}\sqrt{(l+k)}}, \quad (23)$$

a result already obtained by Prof. Spearman and by Mr. Thomson.

We observe that, according to equation (22),  $S$  and  $S'$  (or  $q$  and  $q'$ ) possess not  $l$  independent common factors, but *one* only. For by a linear transformation of independent variables such as is given by equations (3) to (7) above, we might take  $\xi = \frac{1}{\sqrt{(l)}}(x_1 + x_2 + \dots + x_l)$ , thus replacing  $x_1, x_2, \dots, x_l$  by one variable  $\xi$ , without affecting the other  $m+k$  independent variables,

$$x_{l+1}, x_{l+2}, \dots, x_{l+m}, x_{l+1}', x_{l+2}', \dots, x_{l+k}'.$$

### III.

We shall next show that, when the correlations between  $n$  variables,  $q_1, q_2, \dots, q_n$ , each of which is distributed according to the normal law with the same probable error, satisfy Mr. Burt's conditions, namely,\*

$$\frac{r_{as}}{r_{at}} = \frac{r_{bs}}{r_{bt}}, \quad (24)$$

where  $a, b, s, t$  have any different values from 1 to  $n$  inclusive, the  $q$ 's may be expressed as linear functions of  $n+1$  independent variables, each of which is distributed according to the normal law with the same probable error as that of the  $q$ 's, and one of which is a *single general factor*, while the remainder are specific factors. Following Mr. Burt, we shall speak of the  $\frac{1}{2}n(n-1)$  coefficients that satisfy equations (24) as forming a hierarchy.

From equations (24) it follows that

$$1 = \frac{r_{ab}}{r_{cb}} \cdot \frac{r_{bc}}{r_{dc}} \cdot \frac{r_{cd}}{r_{ab}} = \frac{r_{as}}{r_{cs}} \cdot \frac{r_{bs}}{r_{ds}} \cdot \frac{r_{ds}}{r_{as}} \quad (a, b, c, d = 1, 2, \dots, n),$$

so that 
$$\frac{r_{as}r_{bs}}{r_{ab}} = \frac{r_{cs}r_{ds}}{r_{cd}} = \text{etc.}, = f(s), \text{ say,} \quad (25)$$

where  $f(s)$  depends upon  $q_s$  above. Now suppose that the absolute magnitude of  $r_{12}$  is greater than that of any of the other correlations, and that  $r_{12}^2 \geq r_{13}^2 \geq r_{14}^2 \geq \dots \geq r_{1n}^2$ . Then, in general, equations (24) give

$$\frac{r_{ak}^2}{r_{s \cdot (k+1)}^2} = \frac{r_{1k}^2}{r_{1 \cdot (k+1)}^2} \leq 1,$$

so that 
$$\{f(s)\}^2 = \frac{r_{as}^2 r_{bs}^2}{r_{ab}^2} = \frac{r_{1s}^2 r_{2s}^2}{r_{12}^2} \leq 1.$$

\* BURT, *loc cit.*, p. 159.

Moreover,

$$\frac{f(s)}{f(t)} = \frac{r_{as}r_{bs}}{r_{at}r_{bt}} = \frac{r_{as}^2}{r_{at}^2}$$

from equation (24). It follows that the absolute magnitude of  $f(s)$  lies between zero and unity, and that the sign of  $f(s)$  is the same as that of  $f(t)$  for all values of  $s$  and  $t$  from 1 to  $n$  inclusive. Since every suffix occurs twice in equations (24), these equations would not be affected if we were to change the sign of the unit in terms of which any one (or more) of the  $q$ 's is measured. We may therefore so choose the signs of the units in terms of which  $q_2, q_3, \dots, q_n$  are measured that  $r_{12}, r_{13}, \dots, r_{1n}$  are all positive. Then, since

$$f(s) = \frac{r_{1s}r_{st}}{r_{1t}},$$

and every  $f(s)$  has the same sign,  $r_{st}$  will have the same sign for all values of  $s$  and  $t$  from 2 to  $n$  inclusive, and this sign will be the same as that of  $f(s)$  for all values of  $s$  from 1 to  $n$ . It follows that, if the signs of the units in terms of which  $q_2, q_3, \dots, q_n$  are measured be so chosen that all the  $r$ 's in the first row or column of the correlation table

$$\left. \begin{array}{cccccc} & r_{12} & r_{13} & \dots & r_{1n} & \\ r_{12} & - & r_{23} & \dots & r_{2n} & \\ r_{13} & r_{23} & - & \dots & r_{3n} & \\ \vdots & \vdots & \vdots & & & \\ r_{1n} & r_{2n} & r_{3n} & \dots & - & \end{array} \right\} \quad (26)$$

are positive,  $f(s)$  will be positive for all values of  $s$ , unless every  $r$  outside the first row and column is negative, a condition that is not fulfilled, so far as the present writer has been able to ascertain, by any table of correlations between mental tests that has hitherto been published. We shall therefore take it that  $f(s)$  is positive for all values of  $s$  when equations (24) are satisfied by the correlations between  $n$  mental tests.

Since, then,  $0 \leq f(s) \leq 1$ , we may write

$$\sqrt{\{f(s)\}} = r_{sg} = \cos gOq_s \quad (s = 1, 2, \dots, n), \quad (27)$$

on the analogy of equation (17), where  $r_{sg}$  is the correlation between  $q_s$  and some  $(n+1)$ th variable,  $g$ , that is also distributed according to the normal law with the same probable error as before. Now, it may be shown that  $n$  correlated  $q$ 's, each of which is distributed according to the normal law with the same probable error, can always be expressed with  $\frac{1}{2}n(n-1)$  degrees of freedom, in terms of  $n$  independent variables  $\xi_1, \xi_2, \dots, \xi_n$ , each of which is distributed according to the normal law with the same probable error as before, by means of equations (8). Thus

$$\left. \begin{array}{l} q_s = \mu_1 \cdot \xi_1 + \mu_2 \cdot \xi_2 + \dots + \mu_n \cdot \xi_n \\ \mu_1^2 + \mu_2^2 + \dots + \mu_n^2 = 1. \end{array} \right\} \quad (28)$$

We may therefore regard  $l_1, l_2, \dots, l_n$  as direction-cosines (or as "correlation-cosines," since  $l_i$  is the coefficient of correlation between  $q_i$  and  $\xi_i$ ) of a line  $Oq_s$  drawn through the origin in  $n$ -dimensional space, and making with the axis  $O\xi_i$  an angle equal to  $\cos^{-1}l_i$ . We can, therefore, draw, in  $(n+1)$ -dimensional space, a line  $Oq$  making given angles with each of the  $n$  lines  $Oq_1, Oq_2, \dots, Oq_n$ . And since (unless the italicised condition in the previous paragraph were satisfied)  $f(s)$  is positive and less than unity, we may take these  $n$  angles to be  $\cos^{-1}\sqrt{\{f(s)\}} = \cos^{-1}r_{sg}$ , etc., say, where  $s = 1, 2, \dots, n$ ; so that, according to equation (17),  $r_{sg}$  is the correlation between  $q_s$  and a new  $([n+1]\text{th})$  quality  $q_g$ , that is distributed according to the normal law with still the same probable error.\*

By means of a transformation of independent variables such as is given in equations (3) to (7) let us now express our  $n+1$  qualities  $q_1, q_2, \dots, q_n, q_g$  in terms of new independent variables  $y_1, y_2, \dots, y_n, y_{n+1}$ , distributed as before, and let us choose  $y_{n+1} \equiv q_g$ . Then, in place of equations (28) we have

$$q_s = r_{sg} \cdot q_g + {}_sm_1 \cdot y_1 + {}_sm_2 \cdot y_2 + \dots + {}_sm_n \cdot y_n, \quad (29)$$

where

$$r_{sg}^2 + {}_sm_1^2 + {}_sm_2^2 + \dots + {}_sm_n^2 = 1 \quad (30)$$

for all values of  $s$  from 1 to  $n$  inclusive. Equation (16) then gives

$$r_{st} = r_{sg}r_{tg} + {}_sm_1 \cdot {}_tm_1 + {}_sm_2 \cdot {}_tm_2 + \dots + {}_sm_n \cdot {}_tm_n \quad (s, t = 1, 2, \dots, n). \quad (31)$$

But

$$\begin{aligned} r_{sg}r_{tg} &= \sqrt{\{f(s) \cdot f(t)\}} = \sqrt{\left(\frac{r'_{as}r'_{bs}}{r'_{ab}} \cdot \frac{r'_{at}r'_{bt}}{r'_{ab}}\right)} \\ &= \sqrt{\left(\frac{r'_{st}r'_{bs}}{r'_{bt}} \cdot \frac{r'_{at}r'_{bt}}{r'_{bs}}\right)} \\ &= r_{st}; \end{aligned} \quad (32)$$

so that equation (31) gives

$${}_sm_1 \cdot {}_tm_1 + {}_sm_2 \cdot {}_tm_2 + \dots + {}_sm_n \cdot {}_tm_n = 0 \quad (s, t = 1, 2, \dots, n). \quad (33)$$

If, therefore, we write

$$x_s = \frac{1}{\sqrt{(1-r_{sg}^2)}} ({}_sm_1 \cdot y_1 + {}_sm_2 \cdot y_2 + \dots + {}_sm_n \cdot y_n) \quad (s = 1, 2, \dots, n), \quad (34)$$

equation (8) shows that  $x_1, x_2, \dots, x_n$  will be variables distributed as before, since, according to equation (30), the sum of the squares of the coefficients of the  $y$ 's is unity. Moreover, from equations (33) it follows that the  $x$ 's are independent of one another; and, since they depend only on the  $y$ 's which

\* In order that it may be possible to draw  $Oq_g$  making given angles,  $\cos^{-1}r_{sg}$  ( $s = 1, 2, \dots, n$ ), with the  $n$  lines  $Oq_s$  ( $s = 1, 2, \dots, n$ ) the sum of the two angles  $q_sOq_g$ ,  $q_tOq_g$  must not be less than the angle  $q_sOq_t$  ( $s, t = 1, 2, \dots, n$ ); that is  $r_{sg}^2 + r_{tg}^2 + r_{st}^2 - 2r_{sg}r_{tg}r_{st}$  must be  $\leq 1$ ; or  $(1-r_{sg}^2)(1-r_{tg}^2)$  must be  $\geq 0$ , since, as we are about to see,  $r_{sg} = r_{sg}r_{tg}$ ; and this last inequality is always satisfied, since  $r_{sg}^2 \leq 1$  ( $s = 1, 2, \dots, n$ ).



are independent of  $q_g$ , they also are independent of  $q_s$ . Substituting from equation (34) in equation (39), and writing  $x_g$  for  $q_g$  in that equation, we obtain

$$q_s = r_{sg} \cdot x_g + \sqrt{(1-r_{sg}^2)} \cdot x_s \quad (s = 1, 2, \dots, n), \quad (35)$$

in which  $x_1, x_2, \dots, x_n, x_g$  are  $n+1$  independent variables, each of which is distributed according to the normal law with the same probable error as that of the  $q$ 's, and among which  $x_g$  is a *single general factor*,\* while all the other  $x$ 's are specific factors. There are no group factors.

## IV.

We have now to examine the consequences of the fulfilment of Prof. Spearman's conditions that the correlation between every pair of columns (or rows) in the table

$$\left. \begin{array}{cccccc} & r_{12} & r_{13} & \dots & r_{1n} \\ r_{12} & & r_{23} & \dots & r_{2n} \\ r_{13} & r_{23} & & \dots & r_{3n} \\ \vdots & \vdots & \vdots & & \vdots \\ r_{1n} & r_{2n} & r_{3n} & \dots & \end{array} \right\} \quad (26)$$

is  $\pm 1$ , where  $r_{st}$  ( $s, t = 1, 2, \dots, n$ ) is the Bravais-Pearson coefficient of correlation between  $q_s$  and  $q_t$ , being any two of  $n$  correlated variables each of which is distributed according to the normal law with the same probable error.

We first observe that, if the correlation between any two sets of quantities

$$x_1, x_2, \dots, x_s, \dots, x_n,$$

$$y_1, y_2, \dots, y_s, \dots, y_n$$

(where  $x_s, y_s$  are corresponding values) is  $\pm 1$ , then  $y_s = Ax_s + B$ . For let bars denote mean values and put  $\xi_s = x_s - \bar{x}$ ,  $\eta_s = y_s - \bar{y}$ . Then we have

$$\pm 1 = \frac{\sum \xi_s \eta_s}{\sqrt{(\sum \xi_s^2 \cdot \sum \eta_s^2)}};$$

so that

$$(\sum \xi_s^2)(\sum \eta_s^2) - (\sum \xi_s \eta_s)^2 = 0,$$

or

$$\sum_{s,t} (\xi_s \eta_t - \xi_t \eta_s)^2 = 0,$$

whence

$$\xi_s / \eta_s = \xi_t / \eta_t \quad (s, t = 1, 2, \dots, n);$$

that is

$$\frac{x_s - \bar{x}}{y_s - \bar{y}} = \frac{x_t - \bar{x}}{y_t - \bar{y}} = \dots = \frac{x_s - x_t}{y_s - y_t} \quad (s, t = 1, 2, \dots, n).$$

It follows that

$$y_s = Ax_s + B \quad (s = 1, 2, \dots, n), \quad (36)$$

where A and B are constants independent of  $s$ .

\* It will be remembered that if the italicised condition on p. 100 were not satisfied  $r_{sg}$  would be imaginary.

Consider then the four coefficients,  $r_{as}$ ,  $r_{at}$ ,  $r_{bs}$ ,  $r_{bt}$  in table (26), where  $a$ ,  $b$ ,  $s$ ,  $t$  have any different values from 1 to  $n$  inclusive.

Equation (36) applied first to the  $a$ th and  $b$ th columns and then to the  $s$ th and  $t$ th columns (between each which two pairs of columns the correlation is  $\pm 1$ ), gives us, first,

$$r_{bs} = A_{ab}r_{as} + B_{ab}, \quad (37)$$

$$r_{bt} = A_{ab}r_{at} + B_{ab}, \quad (38)$$

where  $A_{ab}$ ,  $B_{ab}$  depend on  $a$  and  $b$  alone, and then

$$r_{at} = A_{st}r_{as} + B_{st}, \quad (39)$$

$$r_{bt} = A_{st}r_{bs} + B_{st}, \quad (40)$$

where  $A_{st}$ ,  $B_{st}$  depend on  $s$  and  $t$  alone. From the second and third of these equations we obtain

$$r_{bt} = A_{ab}A_{st}r_{as} + A_{ab}B_{st} + B_{ab},$$

while the first and fourth equations give

$$r_{bt} = A_{ab}A_{st}r_{as} + A_{st}B_{ab} + B_{st}.$$

Subtracting one of the last two equations from the other,

$$0 = B_{ab}(A_{st}-1) - B_{st}(A_{ab}-1),$$

so that

$$\frac{B_{ab}}{A_{ab}-1} = \frac{B_{st}}{A_{st}-1} = C, \text{ say,}$$

where  $C$  is a constant independent of  $a$ ,  $b$ ,  $s$ ,  $t$ . Equation (37) now becomes

$$r_{bs} + C = A_{ab}(r_{as} + C);$$

so that the four equations (37) to (40) may be replaced by

$$\frac{r_{as} + C}{r_{at} + C} = \frac{r_{bs} + C}{r_{bt} + C} \quad (a, b, s, t = 1, 2, \dots, n), \quad (41)$$

relations resembling Mr. Burt's conditions for a hierarchy.

Equation (41) gives

$$C = \frac{r_{at}r_{bs} - r_{as}r_{bt}}{r_{as} - r_{bs} - r_{at} + r_{bt}} \quad (a, b, s, t = 1, 2, \dots, n). \quad (42)$$

If we alter the signs of the units in terms of which  $q_s$  and  $q_t$  are measured, without altering the signs of the units in terms of which  $q_a$  and  $q_b$  are measured, we shall alter the sign of  $C$  without affecting the fulfilment of the condition that the correlation between every pair of columns in the table (26) is  $\pm 1$ . We may therefore assume that  $C$  is positive and equal to  $k^2$ , say.

Now suppose that

$$q_s = \lambda_1 \cdot \xi_1 + \lambda_2 \cdot \xi_2 + \dots + \lambda_N \cdot \xi_N; \text{ and } \lambda_1^2 + \lambda_2^2 + \dots + \lambda_N^2 = 1, \quad (43)$$

where  $\xi_1, \xi_2, \dots, \xi_N$  ( $N \geq n$ ) are independent variables, each distributed according to the normal law, with the same probable error as that of the  $q$ 's. Let us

now introduce a new set of independent variables,  $\xi'_1, \xi'_2, \dots, \xi'_N$ , defined by

$$\xi_1 = h\xi'_1, \xi_2 = h\xi'_2, \dots, \xi_N = h\xi'_N, \quad (44)$$

in which, as will appear from equation (48) below,  $h$  is a real quantity, intermediate in value between  $\pm 1$ ; and let us put

$$q'_s = h(l_1 \cdot \xi'_1 + l_2 \cdot \xi'_2 + \dots + l_N \cdot \xi'_N) - \sqrt{(1-h^2)} \cdot \xi' \quad (s = 1, 2, \dots, n) \quad (45)$$

$$= q_s - \sqrt{(1-h^2)} \cdot \xi' \quad (s = 1, 2, \dots, n), \quad (46)$$

where  $\xi'$  is a variable, independent of  $\xi'_1, \xi'_2, \dots, \xi'_N$ , but distributed according to the normal law, with the same probable error as  $\xi'_1, \dots, \xi'_N$ . Then it follows from equation (45), in which the sum of the squares of the coefficients of the  $\xi'$ 's is equal to unity, that  $q'_s$  (where  $s$  has any value from 1 to  $n$  inclusive) is distributed according to the normal law, with the same probable error as the  $\xi'$ 's, but a different probable error from that of the  $q$ 's and  $\xi$ 's.

Using equations (45), we obtain from equation (16) an expression for the correlation,  $r'_{st}$ , between  $q'_s$  and  $q'_t$ , namely,

$$r'_{st} = h^2(l_1 \cdot l_1 + l_2 \cdot l_2 + \dots + l_N \cdot l_N) + (1-h^2) \quad (47)$$

$$= h^2 r_{st} + (1-h^2) = h^2(r_{st} + C) = h^2(r_{st} + k^2), \quad (48)$$

if  $h^2 = \frac{1}{1+k^2}$ , from which it follows that  $h^2$  is positive and less than unity.

From equations (48) combined with equations (41) we now obtain

$$\frac{r'_{as}}{r'_{at}} = \frac{r'_{bs}}{r'_{bt}} \quad (a, b, s, t = 1, 2, \dots, n),$$

so that the correlations between the  $q'$ 's satisfy Mr. Burt's conditions expressed in equations (24). It follows from equations (35) that

$$q'_s = l_s \cdot x'_g + \sqrt{(1-l_s^2)} x'_s \quad (s = 1, 2, \dots, n), \quad (49)$$

where  $l_s = r'_{sg},^*$  (50)

and where  $x'_g$  is a single general factor of  $q'_1, q'_2, \dots, q'_n$ , while  $x'_s$  is a specific factor of  $q'_s$ . Here  $x'_g$  and  $x'_s$  ( $s = 1, 2, \dots, n$ ) are distributed according to the normal law, with the same probable error as that of the  $q'$ 's. Substituting from equations (46), we now obtain

$$\begin{aligned} q_s &= q'_s + \sqrt{(1-h^2)} \cdot \xi' \\ &= l_s \cdot x'_g + \sqrt{\left(\frac{k^2}{1+k^2}\right)} \cdot \xi' + \sqrt{(1-l_s^2)} \xi'_s; \end{aligned}$$

which, if  $hx'_g = x_g, h\xi' = y, hx'_s = x_s$  ( $s = 1, 2, \dots, n$ ) (51)

becomes

$$q_s = x_g \cdot l_s \sqrt{(1+k^2)} + y \cdot k + x_s \cdot \sqrt{\{(1-l_s^2)(1+k^2)\}} \quad (s = 1, 2, \dots, n), \quad (52)$$

\* The words in italics on p. 100 indicate that, under certain conditions,  $l_s = r'_{sg}$  might become imaginary. But these conditions do not appear to be fulfilled in the case of correlations between mental tests.

$$\text{or } q''_s = (q_s - y \cdot k) \frac{1}{\sqrt{(1+k^2)}} = l_s \cdot x_s + \sqrt{(1-l_s^2)} \cdot v_s \quad (s=1, 2, \dots, n) \quad (53)$$

for all values of  $s$  from 1 to  $n$  inclusive. A comparison of equations (44) and (51) shows that  $x_s$ ,  $y$ , and  $v_s$  ( $s=1, 2, \dots, n$ ) are variables distributed according to the normal law, with the same probable error as that of the  $q$ 's. Moreover,  $y$  is independent of the  $q$ 's, while the  $x$ 's in equations (52) and (53) are  $n+1$  independent variables, of which  $x_y$  is a single general factor of the  $n$  expressions on the left-hand sides of equations (53), while  $v_s$  is a specific factor of the expression on the left of the  $s$ th equation. Finally,  $q''_s$  in equations (53) is proportional to  $q'_s$ , being given by  $q'_s = q''_s \sqrt{(1+k^2)}$ , so that the correlations of the  $q''$ 's are the same as of the  $q'$ 's; and the  $q''$ 's are distributed according to the normal law, with the same probable error as that of the  $q$ 's.

We conclude that if the correlation between every pair of columns in a table of coefficients of correlation between  $n$  variables  $q_1, q_2, \dots, q_n$  (each of which has a normal probability distribution, with the same probable error) is  $\pm 1$ , then the difference between the  $n$   $q$ 's and a constant multiple  $k$  (which becomes zero when Mr. Burt's conditions for a hierarchy are fulfilled by the correlations of the  $q$ 's) of an  $(n+1)$ th variable  $y$  (that is independent of the  $q$ 's, but distributed according to the normal law with the same probable error) may be expressed in terms of  $n+1$  independent factors (distributed according to the normal law with still the same probable error), of which one is a single general factor, while the remaining  $n$  are specific factors. There are no group factors.

When  $k=0$  equations (52) or (53) become the same as equations (35), in which case the  $q$ 's will be expressible in terms of  $n+1$  independent variables, each of which is distributed according to the normal law, and one of which is a single general factor, while the others are specific factors. Equation (42) shows that  $C$  and  $k$  will be zero whenever Mr. Burt's conditions for a hierarchy are satisfied, unless indeed  $r_{aa} + r_{bt} = r_{bs} + r_{at}$  for all values of  $a, b, s, t$  from 1 to  $n$  inclusive. It is evident that, if the correlations in table (26) represent the correlations between a sufficiently large number of sufficiently dissimilar mental tests, the average correlation between any one test and all others will be zero, and  $C$  and  $k$  will consequently vanish. It follows that, if the correlation between every pair of columns in a correlation table representing the results of a large number of *sufficiently dissimilar* mental tests be  $\pm 1$ , the measures of the correlated qualities can be expressed by means of equations (35), in terms of a single general factor and specific factors only. There will be no group factors.

## V.

We now return to the consideration of equation (18), which gives the condition that three qualities  $Q_1$ ,  $Q_2$ , and  $Q_3$  should depend upon two independent variables and upon two only. Our equation was :

$$\cos^{-1} r_{23} + \cos^{-1} r_{31} + \cos^{-1} r_{12} = 0, \quad (18)$$

where, if  $X$  and  $Y$  are the two independent variables in question, the measurements of  $Q_1$ ,  $Q_2$ , and  $Q_3$  are given by

$$\left. \begin{aligned} q_1 &= x \cos \theta_1 + y \sin \theta_1 \\ q_2 &= x \cos \theta_2 + y \sin \theta_2 \\ q_3 &= x \cos \theta_3 + y \sin \theta_3 \end{aligned} \right\} \quad (54)$$

Dr. Webb, in his paper on "Character and Intelligence" describes an investigation of 48 mental qualities. The subjects of his enquiry were 98 men students (average age 21) at a training college during the last six months of their second year of training (January to July, 1912), and a similar group of 96 students during the corresponding period of the following year (January to July, 1913). Of the students' 48 mental qualities investigated, 43 were estimated by pairs of prefects who acted as judges; to each pair a group of 20 (or 19) students was assigned. The measurements of the qualities were so chosen as to give the same constant to the frequency distribution of each.\* The 43 mental qualities estimated by the prefects included the following, described in Dr. Webb's schedule under the head 'Intellect':†

No. 35. Quickness of apprehension.

36. Profoundness of apprehension.

37. Soundness of common-sense.

38. Originality of ideas.

Among the five qualities not estimated by the prefects, two were objectively measured, namely, Examinational Ability and the general factor—General Ability—whose measure is  $g$ .‡ The manner in which  $g$  was measured is fully described in Dr. Webb's paper. Following Dr. Hart and Prof. Spearman, Dr. Webb described ' $g$ ' as a "General Factor of Intellective Energy";§ but Dr. Webb produces no additional evidence for regarding  $g$  as a measure of intellective energy rather than as, for example, a measure of power of

\* See footnote †, p. 93.

† *Loc. cit.*, pp. 18 and 19.

‡ It will be remembered that  $g$ , like the measures of the other qualities with which we are concerned, is distributed according to the normal law, and may have any value  $-\infty$  to  $+\infty$ , its mean value being zero. For brevity we shall, for the future, commonly write ' $g$ ' instead of "the quality whose measure is  $g$ ."

§ *Loc. cit.*, p. 37.

voluntarily concentrating nervous energy, or, what amounts to the same thing, voluntarily concentrating attention.

The correlations of  $g$  with the four intellectual qualities\* just enumerated lie between 0.29 and 0.56. The qualities in question are not, therefore, functions of  $g$  alone. Dr. Webb observes that these correlations "are certainly high and significant, and among the highest correlations of  $g$  with any of the estimates, but the question naturally arises why they are not higher—the inter-correlations among the estimates themselves reaching in all cases over 0.80."† Dr. Webb, noticing that the correlation of quality No. 8—"Degree of Sense of Humour"—with  $g$  was very small ( $-0.17$ ), while its correlations with the four qualities enumerated above are respectively 0.85, 0.49, 0.45 and 0.79, tried the effect of eliminating the influence of "Humour" from the correlations between  $g$  and the prefects' estimates of the four intellectual qualities enumerated. For this purpose Yule's formula, obtained in equation (20) above, was used. The four partial correlations thus calculated were respectively 1.16, 0.75, 0.42, and 1.00. It follows that not only ' $g$ ,' but some other quality or qualities independent of ' $g$ ,' one or more of which is connected with Humour, enter into the prefects' estimates of the four intellectual qualities. Moreover, the fact that, when the effect of variation of Humour is eliminated, the partial correlations between ' $g$ ' and Quickness, as well as between ' $g$ ' and Originality, are approximately +1, suggests that each of the four qualities—' $g$ ,' Humour, Originality and Quickness—depends upon two independent variables and upon two only.

Let us denote these four qualities by  $Q_g$ ,  $Q_h$ ,  $Q_o$ , and  $Q_q$  respectively. According to equation (18), if the first three of these depend upon two independent factors, and upon two only,

$$\cos^{-1} r_{ho} + \cos^{-1} r_{og} + \cos^{-1} r_{gh} = 0. \quad (55)$$

Dr. Webb's table of corrected coefficients between all the 48 qualities involved in his investigation gives

$$r_{ho} = .79; \quad r_{og} = .17; \quad r_{gh} = -.17;$$

so that

$$\cos^{-1} r_{ho} = \pm 37^{\circ} 82; \quad \cos^{-1} r_{og} = \pm 61^{\circ} 97; \quad \cos^{-1} r_{gh} = \pm 99^{\circ} 81.$$

If we take the same sign for the first two and the other sign for the last of these angles, we have

$$\cos^{-1} r_{ho} + \cos^{-1} r_{og} + \cos^{-1} r_{gh} = \pm 0^{\circ} 02, \quad (56)$$

which differs from zero by much less than the probable error. We conclude

\* Here, and often in the sequel, the word "quality" is used for brevity, to denote the measure of the same quality.

† *Loc. cit.*, p. 43.

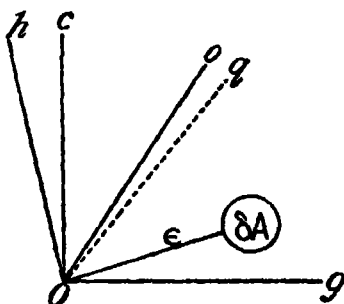
that 'g,' as determined experimentally, and Humour and Originality, as estimated in a very large number of cases by Dr. Webb's collaborators, are compounded of two, and two only, independent factors.

Let us now construct a diagram by drawing lines  $Og$ ,  $Oh$ ,  $Oo$  in one plane, making the following angles with each other:—

$$gOh = \cos^{-1} r_{go} = 100^\circ,$$

$$hOo = \cos^{-1} r_{ho} = 38^\circ,$$

$$oOg = \cos^{-1} r_{og} = 62^\circ.$$



If we would see whether the axis of Quickness,  $Oq$ , lies in the same plane as the axes of 'g,' Humour and Originality, we obtain from Dr. Webb's table

$$r_{gg} = .53; \quad r_{gh} = .85; \quad r_{go} = 1.04 = 1.0;$$

so that

$$\cos^{-1} r_{gg} = \pm 58^\circ; \quad \cos^{-1} r_{gh} = \pm 32^\circ; \quad \cos^{-1} r_{go} = \pm 0^\circ.$$

We obtain from equation (18), if, as before, we take the two smaller angles with one sign and the larger angle with the other sign,

$$\cos^{-1} r_{gh} + \cos^{-1} r_{hg} + \cos^{-1} r_{gg} = \pm 10^\circ,$$

$$\cos^{-1} r_{go} + \cos^{-1} r_{og} + \cos^{-1} r_{gg} = \pm 4^\circ,$$

$$\cos^{-1} r_{gh} + \cos^{-1} r_{ho} + \cos^{-1} r_{og} = \pm 6^\circ.$$

We may take it, then, that the axis of Quickness lies very nearly, if not quite, in the same plane as the three axes of 'g,' Humour and Originality. Or, in other words, Quickness consists almost entirely, if not quite, of some combination of the same two independent factors as constitute the other three qualities. We might therefore add to the diagram another line,  $Oq$ , coincident, or almost coincident, with  $Oo$ . The angles  $qOg$ ,  $qOh$ ,  $qOo$  would then be very nearly equal to  $\cos^{-1} r_{gg}$ ,  $\cos^{-1} r_{gh}$ , and  $\cos^{-1} r_{go}$ , as obtained from Dr. Webb's table.

If the Training College students who formed the subjects of Dr. Webb's investigation constitute a fair sample of adult Englishmen, the g, Sense of Humour, Originality, and (probably) Quickness of Apprehension of every Englishman can be represented by a single point on the plane of the diagram—the intellectual plane, as we may perhaps facetiously call it. And the proportion of Englishmen whose intellectual qualities (if for the moment

we may confine this term to the four qualities just named) are represented by points lying within any small area  $\delta A$ , would be equal to the volume of a cylinder having its axis perpendicular to  $\delta A$ , its base on  $\delta A$ , and bounded at its other extremity by the surface

$$z = \frac{1}{2\pi\sigma^2} e^{-(x^2+y^2)/2\sigma^2} = \frac{1}{2\pi\sigma^2} e^{-\epsilon^2/2\sigma^2}, \quad (57)$$

where  $x$  and  $y$  are the measurements of the two independent variables  $X$  and  $Y$  whose axes lie in the plane of the diagram, and where, as in equation (14) above,

$$\epsilon^2 = x^2 + y^2,$$

so that  $\epsilon$  measures the degree in which subjects represented by points in  $\delta A$  are exceptional. Since equation (57) is independent of the particular axes chosen, the number of individuals represented by points in  $\delta A$  is independent of the orientation of the radius joining  $O$  to  $\delta A$ .

Since the equation (57) is independent of the particular axes chosen in the "intellectual" plane, we may choose  $Og$  as one axis. What, then, is the other axis, represented by a line  $Oc$  at right angles to  $Og$ ? Evidently, since the Humour axis makes with it an angle of only some  $10^\circ$ , it is very nearly identical with Humour.

Now Mr. McDougall has suggested that the process of reproduction by similars, or, as William James\* called it, "association by similarity," is due to "a partial identity of the complex neural systems involved in the perception of two objects. Each system consists of many sub-systems, and one or more of these sub-systems is common to the two. When the one system is excited, its excitement spreads, not, as is most commonly the case, through some association-path previously established by some temporal contiguity, but from the sub-system, which forms also a part of another system, radiates itself through that other system. In the commonplace type of mind this process comparatively rarely occurs. It would seem that, in the brains of such persons, neural systems tend to become circumscribed and individualised, whereas in a higher type of brain the neural systems are more complexly interwoven, sub-systems becoming freely associated with many principal systems. In a brain so constituted, reproduction of similars will frequently occur, causing the dull chain of simple reintegration, the serial reproduction of impressions associated by temporal contiguity, to be broken across. The possessor of a brain so constituted will never be a commonplace person; he may be a crank or an original thinker, or merely a wit."†

\* 'Principles of Psychology,' vol. 1, p. 578.

† 'Physiological Psychology,' p. 139.



There is no evident reason why such a constitution of brain should have anything to do with capacity voluntarily to concentrate attention, the capacity which Binet and others have identified with the quality whose measure is  $g$ . Now the quality independent of ' $g$ ' for which we are seeking is very closely connected with Wit or Humour, and also closely connected with Originality. Its correlation with Humour is, as we see from our diagram (p. 108),  $\cos 10^\circ$  or 0.98, and its correlation with Originality is  $\cos 28^\circ$  or 0.88. Let us call it Cleverness. Then Cleverness is defined as a quality, independent of ' $g$ ,' which, combined with ' $g$ ' in different proportions, wholly constitutes Humour or Originality, and wholly or mainly constitutes Quickness of Apprehension. Being closely connected with Humour and with Originality, Cleverness as thus defined is also closely connected with the form of brain constitution described by Mr. McDougall in the passage we have quoted. Moreover, so far as we can see, this form of brain constitution, like Cleverness as just defined, is independent of ' $g$ .' We have, therefore, grounds for identifying it with Cleverness.

If further investigation confirms these conclusions and shows, as appears probable, that, of the two independent qualities measured by  $g$  and  $c$  respectively and here described as Ability and Cleverness, the former alone is educable (although its educability may be innate), the distinction between ' $g$ ' and ' $c$ ' should have important consequences for education.\*

The correlations of Cleverness (' $c$ ') with the 48 qualities investigated by Dr. Webb may be calculated as follows: Let us take the general factor measured by  $g$  and Cleverness measured by  $c$  as two of the independent variables in terms of which any of Dr. Webb's qualities may be expressed. Then the measure of any of his qualities is given by equation (8) which now becomes

$$y = r_{gq} \cdot g + r_{cq} \cdot c + l_3 x_3 + \dots + l_n x_n, \quad (58)$$

where  $x_3, x_4 \dots x_n$  are the remaining independent variables. Any of the qualities represented in our diagram, say Humour, is measured by

$$h = r_{gh} \cdot g + r_{ch} \cdot c = r_{gh} \cdot g + [\sqrt{(1 - r_{gh}^2)}] \cdot c, \quad (59)$$

\* Cf. Dr. Mercier's essay on "Cleverness and Capability," 'Human Temperament,' 1917.

[*Note added, March 27, 1919.*—Cleverness, measured by  $c$ , is a "group factor" which, along with the general factor,  $g$ , enters into the constitution of a group of "intellectual" qualities. From any set of *sufficiently dissimilar* mental tests the correlation-producing effect of  $c$  will tend to disappear, leaving the single general factor  $g$  as the only common factor. The same is true of the "group factor," closely connected with Purpose, discussed in the next section: it is an important common factor in a certain group of "purpose" qualities, but its effect in any set of *sufficiently dissimilar* mental tests tends to be negligible. These questions are more fully discussed in a further paper just completed.]

so that, according to our *cosine law*, equation (16),

$$r_{qh} = r_{gq} \cdot r_{gh} + r_{eq} \cdot \sqrt{(1 - r_{gh}^2)},$$

from which we obtain

$$r_{eq} = \frac{r_{qh} - r_{gq} \cdot r_{gh}}{\sqrt{(1 - r_{gh}^2)}}. \quad (60)$$

All the  $r$ 's on the right-hand side of this equation are given in Dr. Webb's table of corrected coefficients for the students. If we substitute Dr. Webb's values and calculate  $r_{eq}$  for all values of  $q$ , except  $q = h$  and  $q = g$ , we obtain the required series of coefficients of correlation. The highest correlations of Cleverness include those with Cheerfulness (0.97) and Quickness of Apprehension (0.95). It follows that Cleverness may be recognised in practice—as, for example, when interviewing for an appointment a candidate, to whose general ability ( $g$ ) testimonials or examination tests bear witness—by noting his Sense of Humour, general tendency to Cheerfulness (which is perhaps difficult to judge on the occasion of such an interview!), or Quickness of Apprehension.

## VI.

It may be shown that the group\* factor discovered by Dr. Webb to be independent of ' $g$ ' and in some close relation to "persistence of motives" or "Purpose" is independent of Cleverness as well as of ' $g$ .' By adding a third axis at right angles to those of ' $g$ ' and ' $c$ ' in the diagram on p. 108, we may represent the extent to which a given individual possesses all three independent factors, and any other quality wholly dependent upon those three, by a single point in a three-dimensional diagram. It will be found that, when a person's "representative point" in this diagram has been determined, a surprisingly large proportion, but of course by no means the whole, of his moral as well as of his intellectual qualities have also been defined.

It is even possible to classify certain important types of character according to the region occupied in such a three-dimensional diagram by the representative point that corresponds to each character in question in so far as that character depends upon the three independent factors, two of which we have called Ability and Cleverness, and of which the third is closely related to Purpose.

\* See preceding footnote.

*Note on the Intensity Decrement in the Balmer Series.*

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(Received March 13, 1919.)

One of the most remarkable examples of spectrum lines which are common in celestial bodies, but which have hitherto resisted all attempts to reproduce them in the laboratory, is afforded by the higher members of the Balmer series of hydrogen. As many as 29 members of this series have been observed by Dyson\* and Evershed† in the chromosphere of the sun, but the greatest number observed in the laboratory by Ames‡ and by Cornu was only 13, and the last of these were of such a character that it would hardly have been possible to record them without a previous knowledge of their localisation. In many respects the failure to reproduce in the laboratory lines whose chemical origin is known, and which are so prominent in celestial spectra, is even more conspicuous than in the case of the nebular and coronal lines, which cannot yet be referred to any atom known in chemistry, and which may be due to substances which do not, or perhaps cannot, exist under terrestrial conditions.

A further interest has been added to the problem by the important theoretical work of Bohr, whose theory of the production of the Balmer series requires that the space occupied by a hydrogen atom, in the process of emitting lines of the higher members of the Balmer series, is such that these radiations cannot be expected to be visible except under conditions of extremely low pressure. Bohr has pointed out that this view is consistent with the appearance of the lines in celestial spectra, and our inability to produce them under the conditions ordinarily obtaining in the laboratory. Liveing and Dewar§ have found that in a mixture of the more volatile gases of the atmosphere, consisting mainly of neon and helium and containing hydrogen, the Balmer series could be traced as far as the ninth member; and in a recent investigation|| we have made a quantitative comparison of the distribution of intensity in the earlier members of the series in hydrogen, and in neon containing hydrogen as an impurity. This observation of Liveing and Dewar is remarkable, but we have recently found that similar results can be obtained in helium containing hydrogen at pressures so great

\* 'Roy. Soc. Proc.,' vol. 68, p. 33 (1901).

† 'Phil. Trans.,' A, vol. 197, p. 381 (1901).

‡ 'Phil. Mag.,' vol. 30, p. 48 (1890).

§ 'Roy. Soc. Proc.,' vol. 67, p. 467 (1900).

|| 'Phil. Trans.,' A, vol. 217, p. 237.

that, on the theoretical considerations above referred to, it would seem impossible that these radiations should be detected.

*Qualitative Experiments.*

Vacuum tubes of the H type were filled with pure helium at a pressure of 41 mm. of mercury in the usual manner by heating powdered thoriated in a silica side-tube, and allowing the gases evolved to pass into the exhausted tube through a tube containing pieces of fused caustic potash and a U-tube containing charcoal, which was cooled in a vessel containing liquid air. The electrodes of the vacuum tube had not been completely cleared of hydrogen, and when the helium was admitted, a fresh evolution of hydrogen from the electrodes took place. The partial pressure of the hydrogen thus liberated must have been very small, and was, in fact, scarcely noticeable on the U-tube containing mercury which served as a pressure gauge, and which showed a pressure of 41 mm. of mercury. At this pressure, however, the spectrum of hydrogen predominated and far surpassed the helium lines in brilliance. In another series of tubes, which were filled in a similar way, but which contained helium at a pressure less than 1 mm. of mercury, and into which a larger quantity of hydrogen had been admitted by heating a palladium tube connected with the circuit in a Bunsen burner, and which therefore contained a far greater proportion of hydrogen, the helium spectrum was predominant.

The spectra obtained with these tubes at 41 mm. pressure were somewhat surprising. The spectrum was first photographed with a small quartz spectrograph, but the results were disappointing, owing to the fact that in the region more refrangible than about 3850 Å the individual lines were to a great extent masked by a continuous spectrum. A higher dispersion being desirable, the spectrum was photographed with a concave grating spectrograph having a grating of 4 feet radius of curvature and ruled with 20,000 lines to the inch. With this instrument the continuous spectrum was less troublesome, and 12 members of the Balmer series could be seen on the plate. The lines were surprisingly sharp; the last member observed, of wave-length 3722 Å, was very faint, but there was no doubt as to its presence. In this region of the spectrum some of the hydrogen lines might be confused with certain of the higher members of the helium series. In our experiments the helium spectrum was weak in comparison with the hydrogen spectrum, but confusion might be suspected in the case of the hydrogen lines of wave-lengths 3770.7 and 3734.15 Å, the wave-lengths of the helium lines in question being 3770.72 Å (int. 1), and the pair 3733.14 and 3733.00 Å both of int. 1, the wave-lengths and intensities being those of Runge and Paschen. It would be

possible for the hydrogen line at 3734.15 Å to be confused with and enhanced by the helium pair at 3783 Å, since the preceding member in the helium series at 3868 Å appears to be present on the plate, but the hydrogen line at 3770.7 Å cannot be affected by the helium line of the same wave-length, since the preceding line in the helium series is not visible.

At first sight it might appear that under these conditions there was a transfer of energy to the higher members of the series, but the nebulous character of these lines as they appear in pure hydrogen suggests that this may not be the case, but that the energy content of the lines as distinct from the intensity at the maximum may be the same, and that their visibility under these conditions may be due to the fact that the energy is concentrated between a narrow range of wave-lengths, instead of being distributed through a broadened line whose apparent intensity is in consequence vanishingly small. Ames,\* referring to the higher members of the series, states that "these lines were the only nebulous lines in the spectrum, but they were sometimes so faint as to escape notice until looked for."

#### *Quantitative Experiments.*

To obtain further evidence on this point we have made quantitative experiments with a view to determining the distribution of intensity in the lines of the Balmer series under different conditions. These quantitative observations have been necessarily confined to the earlier members of the series, but the conclusion is probably justified that the phenomena which they exhibit will be continued by the members of higher term-number. For this purpose we have compared the spectra of four vacuum tubes, which will be referred to by the letters A, B, C, and D. A contained water-vapour and was connected to a small bulb containing a few pieces of anhydrous calcium chloride and soda lime. It may be mentioned that such tubes are very convenient on account of their permanence, when the earlier members of the Balmer series are required (comparatively free from the secondary hydrogen spectrum), the calcium chloride and soda lime acting as a kind of reservoir of water-vapour at a low pressure. At the time this tube was filled it was sealed off at a pressure of about 7 mm. of mercury. The precise pressure of water-vapour in the tube while it was in use was not known, but it may be safely assumed to have been between 5 and 10 mm. of mercury. B was a tube containing pure hydrogen at a pressure less than 1 mm. C and D have been described above, the former containing helium with hydrogen at a pressure less than 1 mm., and the latter helium with a small quantity of hydrogen at 41 mm. pressure.

\* Ames, *loc. cit.*

The method of determining the relative photographic intensities has been identical with that adopted in previous investigations (*loc. cit.*), in which a wedge of neutral-tinted glass was set in front of the slit of the spectrograph, and the photographic intensities determined from the "heights" of the lines on the plate.

The photographic intensity of a line of wave-length  $\lambda$  is defined by

$$\log_{10}^{-1} \left( d_{\lambda} \frac{h_{\lambda}}{m} \right)$$

according to the theory previously given, where  $h_{\lambda}$  is its height as shown on the enlarged photograph, whose magnification is  $m$ , the change of density per millimetre of the wedge at wave-length  $\lambda$  being denoted by  $d_{\lambda}$ . Absolute intensities of any line photographed on the same plate are proportional to the photographic intensities defined in this manner, and the photographic intensities thus form a sufficient basis for comparison of the behaviour of lines in the same spectrum, relatively to one another, when produced under different conditions of electrical excitation. The wedge was the same as that used in the work described in one of our previous communications (*loc. cit.*), in which we substituted the method of calibration of density per millimetre for that of density at the thick end of the wedge, previously adopted.\* The heights of the Balmer series lines on the enlarged photograph, with the consequent calculation of their photographic intensities, are given in the subjoined tables. Owing to a small error in the adjustments in the process of enlargement, the values of  $m$  were not absolutely identical, the respective values being  $m_a = 2.345$ ,  $m_b = 2.337$ ,  $m_c = 2.326$ , and  $m_d = 2.320$ .

Table I.

		B. Pure hydrogen. Pressure < 1 mm.			D. Trace of hydrogen in helium. Pressure 41 mm.		
$\lambda$ .	$d_{\lambda}$ .	$h_{\lambda}$	$h_{\lambda}d_{\lambda}/m$ .	Phot. int.	$h_{\lambda}$ .	$h_{\lambda}d_{\lambda}/m$ .	Phot. int.
H <sub>a</sub>	0.344	17.0	2.502	318	21.7	3.217	1048
H <sub>b</sub>	0.415	12.0	2.131	135	15.2	2.719	524
H <sub>c</sub>	0.490	8.8	1.740	85.0	9.7	2.040	112
H <sub>d</sub>	0.595	4.3	1.095	12.4	4.8	1.231	17.0
H <sub>e</sub>	0.700	1.9	0.569	3.71	1.6	0.483	3.04

\* 'Phil. Trans.,' A, vol. 216, p. 459.

Table II.

A. H <sub>2</sub> O. Pressure 5-10 mm.				C. Hydrogen and helium Pressure < 1 mm.		
$\lambda$ .	$h_{\lambda}$ .	$h_{\lambda}d\lambda/m$ .	Phot. int.	$h_{\lambda}$	$h_{\lambda}d\lambda/m$ .	Phot. int.
H <sub>2</sub>	15.7	2.303	201	16.8	2.485	305
H <sub>2</sub>	9.4	1.064	46.1	12.7	2.266	184
H <sub>2</sub>	5.1	1.066	11.38	7.7	1.622	41.9
H <sub>2</sub>	1.3	0.320	2.18	3.4	0.809	7.40

On Plate A, H<sub>2</sub> is just visible, and on C it is masked by the strong line of the helium principal series. For convenience of discussion, it is desirable to reduce all the values of the photographic intensities to a uniform standard. This is given in Table III, on the basis of an arbitrary intensity of 100 for H<sub>2</sub>.

Table III.

$\lambda$ .	A. Water-vapour.	B. Pure hydrogen.	C. Hydrogen and helium. Pressure < 1 mm.	D. Trace of hydrogen in helium. Pressure 41 mm.
H <sub>2</sub>	100	100	100	100
H <sub>2</sub>	22.9	42.4	60.3	31.8
H <sub>2</sub>	5.78	17.0	18.7	6.80
H <sub>2</sub>	1.06	3.90	2.42	1.08
H <sub>2</sub>	Just visible	1.17	—	0.184

### *The Hydrogen Spectrum in Water-vapour.*

No exact investigation of the intensities of the hydrogen lines in water-vapour has apparently been made hitherto, and a comparison of Plates A and B gives interesting quantitative data in this connection. Evidently, in comparison with the spectrum of pure hydrogen, Plate B, there is a reduction of intensity in the lines from water-vapour, which increases in a regular manner towards the violet end of the spectrum. In the present instance, with H<sub>2</sub> of the same intensity in both cases, H<sub>2</sub> is reduced almost precisely in the ratio 1/2, H<sub>2</sub> in the ratio 1/3, and H<sub>2</sub> in the ratio 1/4. The actual numbers are no doubt accidental, and dependent on experimental conditions such as the pressure, but the general phenomenon is obviously regular and capable of this simple statement.

Another very prominent feature of this comparison is the remarkable suppression of the secondary spectrum of hydrogen in water-vapour. This is of course well known to occur, but its magnitude has never been measured

Plate B shows this spectrum very strongly, but on Plate A, from water-vapour, only a few of the stronger lines of the secondary spectrum appear, and these are much reduced in intensity relative to the series spectrum. There are visible on the plate from water-vapour the lines of wave-length  $\lambda\lambda$  6122, 6080, 6052, 6018, 5976, 5932, 5884-5888, 5813, 4634, and 4580 Å. We have not, however, thought it desirable in this communication to enter into a quantitative discussion of this phenomenon. The reduction appears to be more or less uniform in order of magnitude throughout the secondary spectrum, but it exhibits selective effects, of which an example is afforded by the two strongest lines of wave-lengths 6018.5 and 4634 Å (the latter is double). Their heights are reduced respectively from 8.5 mm. and 8.8 mm. to 2.8 mm. and 2.5 mm., the values of  $d_\lambda$  being 0.355 and 0.444, and the magnification 2.3. We find that the photographic intensities are reduced in water-vapour in the ratios 1/10.2 and 1/13.2, respectively, showing the presence of a definite selective action, while  $H_\alpha$  is only reduced in the ratio 2/3. Their reduction-ratios relative to  $H_\alpha$  are therefore 6.8 for  $\lambda$ 6018.5, and 8.8 for  $\lambda$ 4634. These give sufficient data as to the order of magnitude of the effect. Owing to the great difference in pressure in the two tubes, it must be emphasised that our results refer to this particular case, for the dependence of the water-vapour spectrum on the pressure has not been investigated in a quantitative manner.

*The Hydrogen Spectrum in Helium at 41 mm. Pressure.*

It has already been pointed out that although in the tubes which were filled with helium at 41 mm. pressure, the hydrogen consisted only of the small amount which came out of the electrodes when a heavy discharge was passed through the tubes, the spectrum of hydrogen was nevertheless predominant, that of helium being relatively very weak. Changes in the distribution of intensity were to be expected under these wholly new conditions, and, in fact, those which occur are somewhat striking.

By comparison of Plates B and D, as exhibited in Table III, where the intensity of  $H_\alpha$  has been taken as 100 in each case, we see that in helium at the high pressure  $H_\beta$  is reduced roughly in the ratio 3/4, as against 2/5 for  $H_\gamma$ , 1/4 for  $H_\delta$ , and 2/13 for  $H_\epsilon$ , showing a progressive reduction of a rapid kind towards the violet end of the spectrum. There is no transfer of energy to the shorter wave-lengths, but an actual transfer in the opposite direction. It therefore seems certain that in our tubes at 41 mm. pressure the observation of the higher members of the series depends on the fact that their low intensity, relative to that in tubes at a lower pressure containing pure hydrogen, is more than compensated for by the fact that they do not



suffer the same degree of broadening under these conditions. This opens up an interesting field for enquiry, for if the broadening (of this type) is due to the electric field of neighbouring charged atoms, which previous investigations have, we believe, established, it would appear that the reduction of the broadening in helium may perhaps afford some clue as to the structure, from certain points of view, of the helium atom.

The transfer of energy to members of lower term-number in water-vapour at 5 to 10 mm. pressure, and in helium at 41 mm. pressure, would appear to accord with the theory of Bohr, which demands the existence, for the production of the higher members, of a considerable number of greatly enlarged atoms, but this would appear to be outweighed by the fact that members of the series having a term-number as high as  $m = 14$  are visible at all such pressures. A precise estimate of the relative intensity which any line should have on this theory is not possible, on the sole basis of the assumptions at present inherent in the theory. But some simple considerations, based on the degree of packing of the atoms in relation to the diameter of Bohr's hydrogen atom in its various stationary states, seem to require further assumptions which we cannot regard as reasonable.

Taking the value of  $N$ , the number of atoms in a cubic centimetre of gas at  $0^\circ \text{C.}$  and 760 mm. pressure, as  $2.75 \times 10^{19}$ , we have  $N_{18^\circ \text{C.} \times 41 \text{ mm. pressure}} = 1.41 \times 10^{18}$ . Thus the mean distance apart of the atoms in our tubes is  $2^{1/3} \times N^{-1/3}$  or  $1.0 \times 10^{-6}$ . Now the normal diameter of Bohr's hydrogen atom ( $\tau = 1$ ) is  $1.06 \times 10^{-8} \text{ cm.}$ , its diameter in the various stationary states being  $1.06 \times 10^{-8} (1^2, 2^2, 3^2, \dots \tau^2 \dots)$ , where  $\tau$  takes a series of integral values, such that, when a line of the spectrum  $\nu = B(1/\tau_1^2 - 1/\tau_2^2)$  is developed, the electron is passing from the state defined by  $\tau_2$  to that defined by  $\tau_1$ . For the 12th member of the Balmer series,  $\tau_2 = 14$ ,  $\tau_1 = 2$ . The presence of this line thus requires the existence of the state  $\tau_2 = 14$  in a sufficient number of atoms, and their diameters when in this state are  $d = 1.6 \times 10^{-8} \times 196 = 2.08 \times 10^{-6}$ . The diameters are therefore larger than the mean distance apart of the surrounding helium atoms, in the ratio of about two to unity. Even for the 10th member of the Balmer series, which is very definitely shown on our plates, the diameter of the atom, according to Bohr's theory, would be  $1.53 \times 10^{-6}$ , or about  $1\frac{1}{2}$  times the mean separation of the atoms. Even if an atom could emit such radiations when in actual contact with another atom, a possibility which could hardly be entertained seriously, the chance of its being able to do so must be vanishingly small, and it cannot be assumed that an atom will expand into the state  $\tau = 14$  or more, whenever it occupies a sufficiently isolated position to do so, for in this case the hydrogen spectrum from such

attenuated sources as the nebulae might reasonably be expected to be concentrated near the limit of the series. In the absence of any theory or experimental data which would give a clue to the energy distribution from a source of infinite attenuation, even an approximate estimate of the probable relative intensities of the higher members under the conditions of our experiments is impossible, but, from the available evidence, we feel justified in concluding that assumptions of a far-reaching character will be needed to explain our results in the light of Bohr's theory. We can at present offer no explanation for the phenomena observed; we fear that they constitute a fresh difficulty of some importance in the construction of any theory of the genesis of spectra.

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*Researches on the Chemistry of Coal. Part I.—The Action of  
Pyridine upon the Coal Substance.*

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(Received March 28, 1919.)

*Introduction.*

The experiments recorded in this paper are part of a research carried out in the Department of Chemical Technology at the Imperial College of Science and Technology, at the instance of the British Association Fuel Economy Committee, with the double object of clearing up certain discrepancies in the work of previous investigators and of gaining further knowledge of the chief types of constituents contained in the coal substance.

One of the authors having recently reviewed at some length the present state of science with regard to the composition of coal in his monograph on "Coal and its Scientific Uses" (pp. 35 to 163 inclusive) there is no need to treat of the matter again at any great length here. Special attention may, however, be drawn to the summarised statements given on pp. 111 to 112 and 124 to 128 (inclusive) of that monograph concerning the results and views of previous workers and the present state of our knowledge with regard to the primary action of heat upon coal.

There is now general agreement amongst chemists that the constituents of the coal substance may be regarded as consisting principally of three distinct types derived respectively from the ligno-celluloses, resins, and proteins contained in the vegetable *débris* from which the coal originated.

These bodies have, during the formation of coal, been subjected first of all to the disintegrating influence of decay and bacterial action, as in modern peat bogs, followed by the combined action, continued through long geological ages, of great pressure and a slowly rising temperature, which latter, however, has probably not exceeded  $300^{\circ}$  C. and may have been considerably less. In these circumstances, the relatively unstable cellulosic and proteid constituents would probably undergo such profound changes as would to a great extent mask their original characters, whilst it might be expected that the more stable resinous constituents would be effected to a considerably less degree.

Hitherto it has not been found possible to devise an experimental method for separating the three types of constituents sufficiently well to permit of more than a partial delineation of their chemical behaviours being made. Strangely enough, also, some investigators have spoken of the coal substance as though it contained only cellulosic and resinic derivatives, ignoring the equally important nitrogenous constituents.

Amongst the methods chiefly employed for separating the said constituents, perhaps the most important has been the action of various solvents, and particularly of pyridine, picoline, quinoline, and aniline, upon the coal substance.

Bedson (in 1899) was the first to draw attention, in a paper before the North of England Institution of Mining Engineers, to the remarkable solvent action of pyridine upon bituminous coals, and subsequently, in 1908, he described the details of his work in this connection in a paper read before the Newcastle-on-Tyne Section of the Society of Chemical Industry.\* Since that time the method has been extensively employed by other investigators chiefly by R. V. Wheeler and his co-workers,† and also by Wahl‡, and Harger.§ Vignon|| has similarly investigated the solvent action of aniline and quinoline upon the coal substance.

Clark and Wheeler (*loc. cit.*) have claimed that if the solvent action of pyridine is supplemented by a subsequent chloroform extraction of the original pyridine extract, a complete separation of the resinic from the cellulosic constituents may be effected. But a critical examination of the analytical data published in their paper leaves some doubt in the mind as to the validity of this conclusion, although doubtless a partial separation can be so effected. Their experimental results also show that there had been some

\* 'Journ. Soc. Chem. Ind.,' p. 147 (1908).

† Burgess and Wheeler, 'Trans. Chem. Soc.,' vol. 99, p. 649 (1911); Clark and Wheeler, *ibid.*, vol. 103, p. 1704 (1913).

‡ 'Compt. Rend.,' vol. 154, p. 1094 (1912).

§ 'Journ. Soc. Chem. Ind.,' p. 389 (1914).

|| 'Compt. Rend.,' vol. 158, p. 1421 (1914).

absorption of oxygen by the material during the extraction processes and, in our opinion, these authors did not sufficiently take into account the nitrogenous constituents of the coal substance in applying their method.

The subsequent independent investigations of Harger, Wahl, Vignon, and others have raised the question as to whether the action of pyridine, and other similar basic solvents, is really a case of ordinary solution, for much of the evidence suggests that it is essentially a depolymerising one. Our own work on the subject supports the view recently put forward by one of us that "besides any ordinary solvent action which pyridine may have upon the resinic constituents, which is probably fairly rapid, it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal substance as a whole."\*

In extracting a coal with pyridine in a Soxhlet apparatus in the manner first described by Bedson, and afterwards (with slight modification) by Wheeler and his co-workers, irregularities are frequently encountered, both in regard to speed and ultimate extent of the solvent action. So marked were these found to be in the cases of certain coals examined that the authors determined to subject the action of pyridine to a close examination, with a view to determining the causes of such irregularities.

#### *Experimental.*

In an extended series of preliminary experiments, the results of which need not here be detailed, it was found:—

(1) That the presence of oxygen has an important retarding action, varying considerably with the nature of the coal, upon the extraction process. This is due to the fact that the coal substance, and any pyridine solutions obtained therefrom, absorb oxygen and undergo oxidation during the extraction process. Also, it was found that the previous "oxygenation" of the coal substance renders it much less susceptible to the solvent action of pyridine. Therefore, in order to obtain comparable results with various coals, it is necessary to exclude access of oxygen during the extraction process, which is best carried out in an inert atmosphere.

(2) That the presence of water in the pyridine used has a strong retarding influence upon its solvent action. On the other hand, the presence of picoline and higher homologues of pyridine affect the solvent action but are less stable. Hence the pyridine should be carefully purified and dehydrated before use, or otherwise discordant results as between various coals may be obtained.

\* 'Coal and its Scientific Uses,' p. 93.

(3) That the degree of fineness of the coal operated upon must also be taken into consideration. The coal itself should be carefully dried beforehand, and then ground until it passes through a standard mesh. This, however, should not be too fine, because after a certain limit of fineness has been passed there is a tendency for the finest particles to be carried over mechanically into the flask of the extraction apparatus during the periodic siphoning. Thus, for example, we have found that in most cases the best results are obtained when the dried sample has been ground so as to pass through a standard mesh of 90 to the linear inch.

(4) It is also preferable, though not essential, to arrange the conditions so as to ensure, as far as possible, equality of temperature in the extraction chamber of the apparatus, and also to maintain a regularity in the rate of siphoning during the extraction process. Hence it is desirable to employ some uniform or standard size of extraction chamber and to lag it efficiently. Also, to have all the temperature conditions well under control, and especially the rate of vaporisation of the solvent.

We will now describe the methods and apparatus employed by us to meet the foregoing requirements.

#### *Purification of the Solvent.*

Commercial pyridine always contains picolines and lutidines, and it also has a strong affinity for water forming hydrates, principally  $C_5H_5N, 3H_2O$  (b.p.  $95^{\circ}C.$ ). That supplied to our laboratory was found to contain only about 40 per cent. of basic substances, the remainder being principally water.

After investigating a number of possible methods of separating the pyridine from its various homologues (such as, for example, by means of their hydrochlorides, zinkchlorides, or their compounds with potassium ferricyanide), all of them were finally abandoned in favour of oxidising these impurities by means of a mixture of nitric and chromic acids.

To 900 c.c. of the crude liquid were added 50 grm. of chromic acid and 100 c.c. of nitric acid, and the mixture was then heated in a reflux apparatus for 18 hours. To the cooled liquid 70 grm. of sodium hydroxide were cautiously added. Care was taken not to allow the liquid to become too hot during these operations, for otherwise a point of sudden decomposition would have been reached involving loss of material and some risk of fire.

The liquid was thereupon filtered and afterwards fractionally distilled. Each fraction was dehydrated by the action of quicklime or sodium hydroxide in the first place, and subsequently by prolonged contact with solid caustic potash. After dehydration the fractions were re-distilled under reduced

pressure, moisture being carefully excluded from the apparatus. Only those fractions boiling at atmospheric pressure between 115° and 117° C. were employed for the subsequent extraction operations.

The purity of the solvent so obtained was always carefully checked by density determinations. Thus, for example :—

Boiling point of fraction.	Density referred to water at 4° C.	Temperature.
° C.		° C.
115-116	0·9855	15·2
115-117	0·9850	13·1

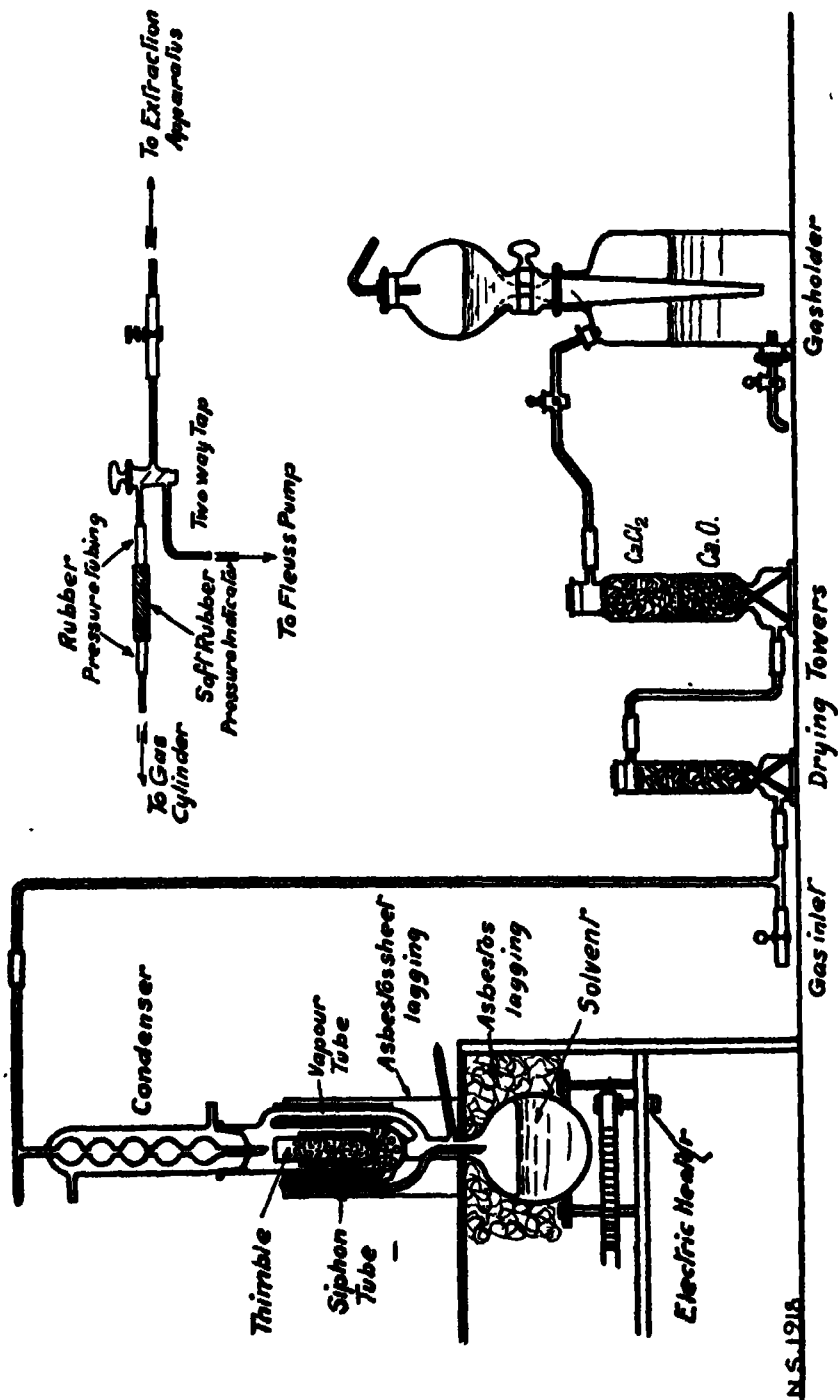
According to Perkin, the density of pure pyridine (b.p. 115·2° C.) referred to water at 4° C. is 0·9855.

#### *Preparation of the Coal Samples.*

The coal was first of all ground so as to pass a mesh of 90 to the linear inch, and then dried in a thin layer in an exhausted desiccator over either concentrated sulphuric acid or phosphoric anhydride. The upper part of the desiccator was fitted with a small electric heater, the radiation from which enabled the temperature of the coal to be raised up to between 80° and 95° C. This greatly accelerated the drying operations without alteration of the coal substance. On the whole, phosphoric anhydride was found to be a more satisfactory drying agent than the sulphuric acid.

#### *The Extraction Apparatus.*

The devising of a satisfactory form of Soxhlet apparatus for the extraction of coal by such solvents as pyridine in an inert atmosphere without inleakage of air was not altogether an easy problem. The chief difficulty encountered was the tendency of pyridine vapour to penetrate in time through even the best ground glass joints that could be made between the evaporation flask and the extraction chamber. And any such escape of pyridine invariably involved a considerable loss of solvent and an inleakage of air at that joint. Finally, it was found necessary to substitute a fused glass joint, which involved making the whole apparatus from the extraction chamber downwards in one piece. No difficulty, however, was encountered in preventing air leakage through a ground glass joint between the extraction chamber and the water-cooled condenser of the apparatus. The final form of apparatus and its connections is shown in the accompanying diagram (fig. 1). The evaporation flask had an external diameter of 9·5 cm., and a capacity of



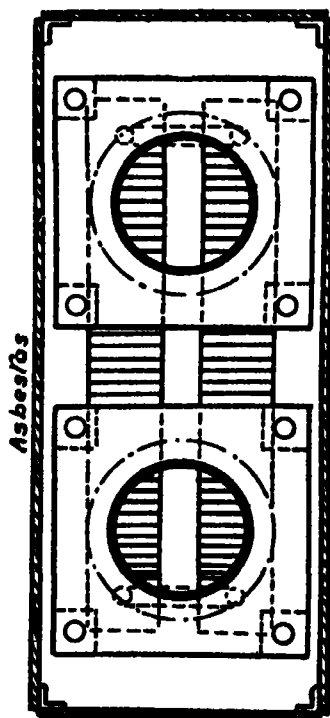
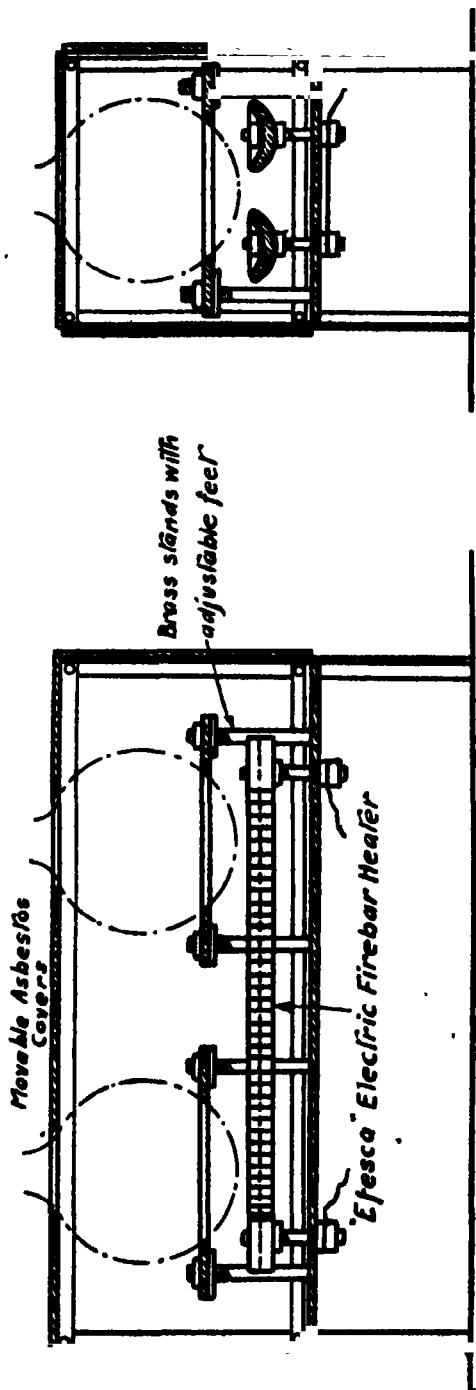


FIG. 2



approximately 450 c.c. The dimensions of the cylindrical extraction chamber were: Length 20 cm., and external diameter 3.7 cm. The water-cooled condenser (length 22 cm., and external diameter 3.7 cm.) contained five bulbs in series.

At the top of the condenser connection was made through two drying towers in series (one of which, 9"  $\times$  1½", contained sticks of solid caustic potash, and the other, 12"  $\times$  2", granulated calcium chloride over lumps of quicklime) to a 2-litre gasholder containing nitrogen over a mixture of equal volumes of glycerine and water.

The extractors were mounted in pairs on an electric heater. Each heater (fig. 2) consisted of a rectangular box of asbestos board screwed on to a

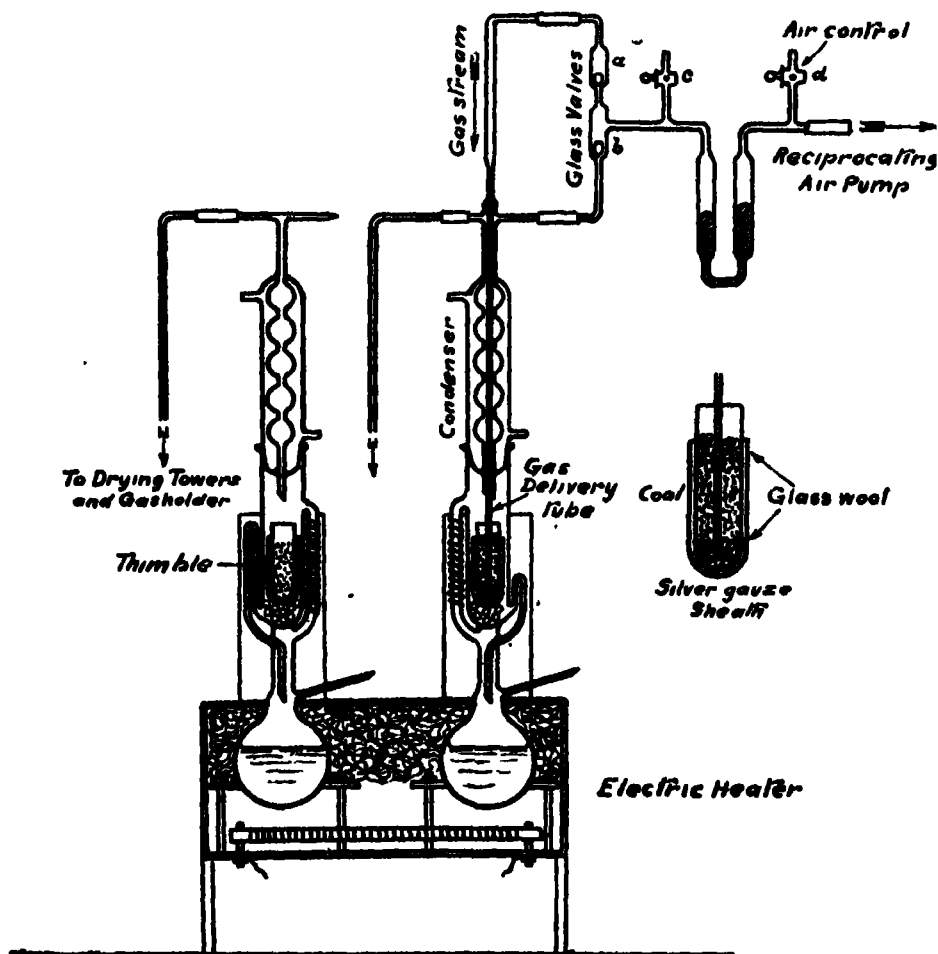


FIG. 3.

framework of angle iron. Two ribbon-wound bar heaters of fireclay, wired for use either in series or in parallel, were placed side by side at the bottom. The flasks of the extractors were supported on brass frames covered with asbestos. The space between the flasks and the sides of the heater was lagged with asbestos wool, the extraction chamber being protected with shaped screens of asbestos board. The arrangement finally adopted of two extraction apparatuses, mounted for parallel experiments in atmospheres of (i) nitrogen and (ii) "moving" oxygen, is shown in fig. 3.

#### *Method of Extraction.*

About 10 grm. of the dried coal was weighed out into a dry paper or alundum thimble.\* The extractor flask was then filled with a measured volume of the pure dry solvent, the thimble placed in the extraction chamber, and the apparatus assembled, a small quantity of lubricant being used to make the ground glass joint tight. The apparatus was then evacuated with the Fleuss vacuum pump, and nitrogen allowed to enter slowly from a cylinder through a reducing valve.† This operation of evacuation and filling was repeated three times, and then the taps on the gasholders were opened to put the extractor in communication with the gas in the holders. Gas samples were then taken and analysed, and if the oxygen present did not exceed 0.5 per cent. the extraction was started. Gas analyses were also made at the end of each operation.

#### *Removal of the Solvent.*

In the subsequent recovery of the extract, the solution was rapidly filtered through a Buchner funnel; the flask was washed out with hot solvent, which, being passed through the filter, served also to dissolve any extract precipitated on cooling. Filtrations through a Gooch crucible were carried out in a jacketed arrangement, which enabled the operation to be done in an atmosphere of nitrogen.

The clear liquid was thereupon concentrated by distillation under reduced pressure. Most of the remaining solvent was removed by alternately heating the residue in the flask from 50° to 60° C. in an atmosphere of nitrogen and evacuating until of constant weight. It was found, however, that this

\* The use of a paper thimble is usually to be preferred, as it ensures a more rapid extraction; the tendency of the paper to break open during a prolonged experiment may be counteracted by strengthening the thimble with a silver gauge sheath, as shown in fig. 3.

† The connections used for these operations are shown in the upper right-hand portion of fig. 1.

treatment failed to remove all the pyridine, and in all our later experiments the concentrated extract was poured into an excess of hydrochloric acid, and was finally collected by filtration through a weighed Gooch crucible, washed, and dried *in vacuo* over strong sulphuric acid.

The insoluble residue in the thimble of extraction chamber was collected, and, after being washed with dry ether, was kept *in vacuo* over strong sulphuric acid with the object of removing any "absorbed" pyridine. But, as will be explained later, so tenaciously was the latter retained, that further special treatment had to be resorted to, before it could all be finally eliminated.

### *Types of Coal Used.*

Our experiments have so far been principally confined to two typical bituminous coals, namely, (i) a Durham "coking" coal, A., and (ii) a Barnsley "hard steam" coal, B., which were selected as having nearly the same percentage compositions, notwithstanding considerable differences in their other properties. Their ultimate compositions were as follows:—

	C.	H.	N.	S.	O.	Ash.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
A. Durham coking coal .....	83.73	4.76	1.09	1.28	7.52	1.62
B. Barnsley hard steam coal	82.88	4.99	1.50	0.70	7.72	2.76

These coals behave quite differently on carbonisation at 950° C. The coal A. intumesces and swells considerably, yielding 26.3 per cent. of volatile matter and a residue of very hard "metallurgical" coke. Coal B., on the other hand, does not swell or go through a stage of intumescence, but yields 32.2 per cent. of volatile matter and a much weaker coke. Moreover, when both were exposed to the action of oxygen at a constant temperature of about 108°, the Barnsley coal absorbed the oxygen more quickly than did the other.

In this connection, it may be stated that a comparative study of the behaviour of the two coals, when separately carbonised at a temperature of 550° C., indicated that B. was relatively richer in cellulosic constituents than was A.

### Part I.—EXPERIMENTS WITH COAL A.

#### (1) *Comparison between the Action of Pyridine and Picolines.*

The object of these experiments was to determine whether or not, on extraction under ordinary pressure in the Soxhlet apparatus,—

(a) There is a limit to the solvent action of pyridine or picolines on the coal substance ; and

(b) There is any difference in either the rate of solvent action, or ultimate proportion of the constituents extracted, by pyridine and picolines respectively.

The pyridine employed was a fraction of the purified anhydrous solvent, boiling between  $115.3^{\circ}$  and  $116.3^{\circ}$ , whilst the picolines were a fraction of anhydrous pyridine homologues boiling between  $130^{\circ}$  and  $150^{\circ}$ . For this purpose the dried coal was continuously extracted in an atmosphere of nitrogen, in the first instance for an uninterrupted period of 159 hours, after which the residue was similarly extracted for a further period of 24 hours.

Experiment.	Solvent.	Percentage of dry coal extracted in	
		159 hours.	183 hours.
A. 1 .....	Pyridine .....	31.84	32.27
A. 2 .....	Picolines .....	30.26	31.20

The above figures show that the amount extracted in the two cases approached the same practical limit, which, it should be noted, exceeds considerably the amount of volatile matter expelled from the coal at  $950^{\circ}$ . There was nothing to show that the picolines acted more quickly than pyridine upon the coal substance ; indeed, owing to the lesser stability of the picolines, pyridine appeared to be the better solvent generally.

The "residues" were subsequently extracted with dry ether to remove any mechanically-held solvent, and afterwards kept in a vacuum over sulphuric acid for 48 hours. After such treatment their weights were 72.3 and 73.2 per cent. respectively of the original dry coal, from which already 32.2 and 31.2 per cent. of material had been extracted by the solvent. The explanation of this is that the coal substance has a marked affinity for the basic solvents employed, the actions of which are not merely those of ordinary solvents, but partake of a chemical character. The best way of removing from such residues the proportions of "combined" pyridine, etc., which they so obstinately retain, is to wash them first with dilute hydrochloric acid and then with ether.

#### *Character of the "Extracts" and "Residues."*

The "extracts" so obtained were resinous powders of dull chocolate brown colour. The "residues" were very hygroscopic powders, dull black in colour.

On carbonisation, the "extracts" passed through a definite stage of intumescence, leaving a very swollen and puffy coke. The "residues," on the other hand, passed through no such stage of intumescence, the carbonised remainder possessing hardly any cohesiveness.

(2) *The Retarding Influence of Oxygen upon the Extraction Process. Parallel Extraction in (i) Nitrogen and (ii) Oxygen.*

The next experiments show how greatly the extraction process with this coal was retarded by the presence of oxygen. In two parallel experiments, carried out simultaneously and under precisely the same conditions, the dry coal was extracted in an atmosphere of (i) nitrogen and (ii) oxygen for a definite time period until the solvent action appeared to have almost ceased in the first-named case. In one pair of experiments the oxygen was continuously circulated in the Soxhlet apparatus by means of a special mercury pump operated by an electric motor and an air-pump (fig. 3). In the other pair of experiments no such artificial movement was imparted to the atmosphere. Seeing that each apparatus was throughout an experiment in free connection with the gasholder containing the nitrogen or oxygen, as the case might be, the gaseous pressure would be kept constant, and any oxygen absorbed would at once be automatically replaced.

As a rule, visible solvent action had almost ceased after about four days, although the experiments were kept on much longer, so as to allow ample time for a practical limit to be reached in each case. In the "oxygen" experiment about 80 c.c. of the gas (equivalent to about 1 per cent. of the weight of the coal substance used) were absorbed during the first four days, and some further absorption occurred during the remainder of the experiments. The following results of two pairs of parallel experiments may be quoted as typical:—

Experiments A. 3 and A. 4. Coal ground to pass mesh 90.

Total Period of Extraction = 11 days 7½ hours.

Experiment.	Atmosphere.	Percentage extracted.
A. 3 .....	Nitrogen .....	29.72
A. 4 .....	Moving oxygen ..	17.08

Experiments A. 9 and A. 10. Coal ground to pass 150 mesh, but not 200.  
Total Period of Extraction = 7 days 2½ hours.

Experiment.	Atmosphere.	Percentage extracted.
A. 9 . . . . .	Nitrogen . . . . .	32·48
A. 10 . . . . .	Oxygen . . . . .	17·75

In addition to the proof thus given of the marked retarding effect of oxygen upon the extraction process, there was also clear evidence of a definite "affinity" of the coal substance, and particularly of the "residue" left in each case, for pyridine. Thus, for example, in the case of A. 9, the "residue," after being washed with dry ether and subsequently kept *in vacuo* over strong sulphuric acid for 23 days, weighed 77·33 per cent. of the original coal substance, although no less than 28·86 per cent. of the latter had been extracted in a first treatment. In the case of A. 10 the "residue" weighed as much as 92·75 per cent. of the original coal treated, although 16·23 per cent. of the latter had been extracted.

(3) *Practical Limit of Pyridine Extraction and Proportion of Extract soluble in Chloroform.*

From the four following experiments, in which the coal was extracted with pyridine in an atmosphere of nitrogen until the process had reached its practical limit, it would appear that the extractable matter amounted to somewhere between 30 and 33 per cent. of the weight of the dry coal, thus:—

	Experiments.				Mean.
	A. 1.	A. 2.	A. 9.	A. 13.	
Percentage extracted . . . . .	32·27	31·20	32·48	30·44	31·60

A composite sample of such extracts was subsequently extracted in the Soxhlet apparatus with chloroform in an atmosphere of nitrogen for a period of two days, when approximately 52 per cent. of its weight was dissolved. The resulting "chloroform" extract certainly contained both nitrogen and sulphur, and could not be regarded as a pure resinous substance, although it was undoubtedly for the most part resinous in character, as was also shown by its action upon a photographic plate at a temperature of 45° to 55°.

The following analytical results show that, whilst the composition of the "residue" left after the pyridine extraction is far removed from that of any "resin" hitherto found in, or associated with, coal (such resins usually contain upwards of 8.0 per cent. of both hydrogen and of oxygen), that of the pyridine-chloroform "extract" (c) does not sufficiently agree with the same to warrant the view that it represents even a nearly pure coal-resin. A method (discovered during the course of another cognate research at the Imperial College) for isolating pure resins from the coal substance will be described in a later communication.

	Percentage composition.						Ratio C/H.
	C.	H.	S.	N.	O.	Ash.	
(a) Original coal	88.73	4.76	1.28	1.09	7.52	1.62	17.60
(b) "Residue" after pyridine extraction	84.14	4.40	0.93	1.86	4.53	4.14	19.12
(c) Pyridine-chloroform "extract"	80.19	5.96	13.95			—	13.44

#### (4) *Character of the Prolonged Action of Pyridine.*

In all the pyridine extraction experiments, evidence was forthcoming that the action, whilst it finally approached the aforesaid "practical limit," never ceased altogether. Generally speaking, the solvent action was marked by the appearance of a distinct reddish colour in the liquid around the thimble in the extraction chamber, and its termination was signified by the disappearance of such discoloration. Now we repeatedly observed during the investigation that, after the coloration had entirely ceased, and the extraction had therefore been suspended, it re-appeared whenever the apparatus had been left standing for several days with the solvent still in contact with the "residue" in the thimble in the nitrogen atmosphere. Thereupon, on resuming the extraction process in the usual manner, the colour would again disappear after a few hours, but would once more reappear on further standing. In one experiment the phenomenon of alternate disappearance and reappearance was repeated no less than 11 times during a period of 53 days in which the coal was intermittently extracted for altogether 13 days and 19 hours, and betweenwhiles left in contact with the solvent at the laboratory temperature. This supports the view that the so-called "solvent action" of pyridine upon the coal substance is really a more complex phenomenon than has usually been supposed, involving, in addition to a rapid dissolving of the "resinous" constituents, a simultaneous and much

slower "unbuilding," or depolymerising, of the whole coal structure, which was thus gradually brought into a more soluble condition.

(5) *Action of Pyridine at 130° to 150° C. under Pressure.*

Confirmation of the foregoing supposition was forthcoming when the coal was subjected to prolonged heating with pyridine at temperatures between 130° and 150° C. in sealed tubes, the air in which had been displaced by nitrogen before sealing. No apparent thermal decomposition, either to the coal or to the solvent, occurred during the operation. After opening the tubes and filtering their contents, the "residues" were repeatedly treated with successive portions of boiling pyridine until no further matter could be so extracted. Finally the "extracts" were removed, washed with dilute hydrochloric acid, and dried. The following results show how greatly the percentage amounts of "extracts" exceeded those previously obtained by the usual Soxhlet method:—

Experiment.	Weight of coal taken.	Volume of solvent used.	Duration of heating in days.	Percentage of dry coal extracted.
	gram.	c.c.		
A. 21 . . . . .	2.01	123	19	57.16
A. 22 . . . . .	2.00	163	26	63.63
A. 23 . . . . .	1.21	129	26	67.63

Part II.—EXPERIMENTS WITH COAL B.

The results of the following experiments demand attention because they are so strikingly different from these similarly obtained with the "isomeric" coal A.

(1) *Parallel Extraction in Atmospheres of (i) Nitrogen and (ii) Oxygen.*

In these experiments, which were carried out in a similar manner to A. 3 and A. 4 (*q.v.*), the dry coal was extracted with pyridine first of all (a) for a period of 2 days and 22 hours, after which the solvent was replaced by a fresh portion, and (b) the process continued for a further period of 46 days and 17½ hours, with the following results:—

Experiment.	Atmosphere.	Duration.	Percentage extracted.
B. 3.....	Nitrogen .....	(a) 2 days 22 hours.	9.12
		(b) 46 " 17½ "	2.49
			—11.61.
B. 4 .....	Oxygen .....	(a) 2 " 22 "	7.64
		(b) 46 " 17½ "	5.43
			—13.07.



Comparing these results with those of A. 3 and A. 4 respectively, it will be seen that whereas the Durham coking coal ("volatiles" = 26.3 per cent.) yielded (in nitrogen) between 30 and 32 per cent. of "extract," the Barnsley coal ("volatiles" = 32.2 per cent.) yielded only 11.6 per cent. of "extract," a fact which sufficiently proves that there is no necessary relationship between the amount of "volatiles" yielded by the coal at 950° C. and its susceptibility to the attack of pyridine. Also, whilst the retarding influence of oxygen upon the latter is again evident in B., it is far less marked than it was in the case of the Durham coal. Indeed, in the case of the Barnsley coal, the amount ultimately extracted in oxygen was a little more than that removed in nitrogen, even after allowance is made for the fact that the larger gross weight of the former is partly due to an absorption of oxygen, as the following analyses show:—

	Percentage composition of extract.					Total carbon extracted per 100 coal.
	C.	H.	N.	O. and S.	Ash.	
B. 3 .....	81.98	5.92	1.50	10.43	0.17	9.5
B. 4 ... .. {	(a) 79.69	5.97	1.48	12.21	0.65	10.3
	(b) 75.37	3.82	1.50	18.74	0.67	

To discover the cause of the great difference between the behaviour of the two coals towards pyridine would probably require a much longer investigation than we have so far been able to make.

It may prove to be connected with another fact, discovered during the present enquiry, that the substance of coal B. apparently had a markedly stronger affinity for pyridine than that of coal A. Indeed, after the ether-washed "residues" had been kept *in vacuo* over sulphuric acid for 19 days they still retained pyridine with such tenacity that their weights always exceeded those of the original coal taken (*e.g.*, by 5.63 per cent. in B. 3 and no less than 9.47 per cent. in B. 4). This stronger affinity would seem to imply that the coal structure would be more easily "unbuilt" in the case of B. than in that of A., and, therefore, whatever proportion of really pyridine-soluble matter B. might contain would probably be more easily extracted, and the retarding influence of oxygen would be proportionately less marked than in the case of A.

It may here be mentioned that, in conformity with the foregoing supposition, the repeated disappearance and reappearance of colour during intermittent extraction, always observed in the coal A. (*q.v.*), was not noticed in the case of B. This again points to the structure of A. being more complex and

difficult to resolve than that of B., and it is possible that the much more pronounced coking properties of the former are attributable to this circumstance. These matters are, however, reserved for further investigation.

**Part III.—THE ACTION OF PYRIDINE UPON "OXYGENATED" COALS A. AND B.**

Seeing that the presence of oxygen has a retarding influence upon the solvent action of pyridine (more marked, however, in the case of coal A. than in that of B.), it seemed desirable to ascertain what would be the influence of "oxygenating" each coal beforehand, but excluding oxygen during the actual extraction.

Both of the coals in question absorb oxygen, forming "oxygenated" products, rather rapidly at temperatures above 80° and, as already stated, coal B. is, under such conditions, more readily oxidised than coal A. For the purposes of these experiments a sample of the "oxygenated" coal was prepared by circulating oxygen over about 90 grm. of the dried coals in question (previously ground to pass a 90-mesh sieve) at a temperature of 108° until between 10 and 11 litres of the gas had been absorbed. In such circumstances, although oxides of carbon and steam were evolved, the greater part of the oxygen remained in combination with the coal substance, producing "oxygenated" coals of the following percentage composition:—

	C.	H.	N.	S.	O.	Ash.
Oxygenated Coal A. ....	79.39	3.92	1.09	1.28	13.27	1.05
Oxygenated Coal B. ....	74.61	4.03	1.33	0.59	16.97	2.47

Ten grm. of each of these "oxygenated" coals were subsequently extracted with pyridine in the Soxhlet apparatus in an atmosphere of nitrogen, parallel experiments being also made simultaneously with the original coal in each case for purposes of comparison. The extractions were carried out (a) in the first instance for a period sufficient to remove the greater part of the extractable constituents, after which (b) the solvent was replaced by a fresh supply and the extraction continued for a further period until the "practical" limit had been well exceeded. The results in each case proved that "combined" is quite as potent as "free" oxygen in retarding the action of the solvent, as the following figures show:—

## Coal A.

	Experiment A. 5 with original coal. (Percentage extracted.)	Experiment A. 6 with oxygenated coal. (Percentage extracted.)
Duration of Extraction Period—		
(a) 108 hours . . . . .	23·90	12·58
(b) 120 „ . . . . .	1·78	3·53
Total . 228 „ . . . . .	25·68	16·06

## Coal B.

	Experiment B. 1. (Percentage extracted.)	Experiment B. 2. (Percentage extracted.)
Duration of Extraction Period—		
(a) 128 hours . . . . .	9·90	8·81
(b) 624 „ . . . . .	1·66	3·28
Total ..... 752 „ . . . . .	11·56	12·09

Comparing now the results of A. 5 and A. 6 with those of A. 3 and A. 4 (recorded on p. 130), it will be seen that the "combined" oxygen in A. 6 retarded the extraction in almost the same degree as did the "free" oxygen in A. 4. The same also applies in the corresponding B. experiments, as a comparison between the results of B. 1(a) and B. 2(a) and those of B. 3(a) and B. 4(a) will show, although the retarding influence in the case of coal B. was so much less pronounced than in the case of coal A.

The further discussion of the bearing of the results recorded in this paper upon the chemistry of the coal substance is reserved for a further communication which will deal with some later developments of the investigation.

*A Study of Catalytic Actions at Solid Surfaces. I.—Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel.*

By E. F. ARMSTRONG, D.Sc., F.I.C., and T. P. HILDITCH, D.Sc. F.I.C.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received March 28, 1919.)

The object of the present communication is, firstly, to compare the behaviour of unsaturated fatty oils towards hydrogen, in presence of finely disseminated nickel, with that of glucosides, towards water, in presence of enzymes; secondly, to emphasise the remarkable analogy that is apparent between these two different types of interaction.

The nature of enzymes and of their action as hydrolytic agents has been fully discussed by one of us,\* in conjunction with H. E. Armstrong.

The main thesis put forward, in the communication referred to, involves the assumption that enzymic hydrolysis is an operation which takes place at the pseudo-solid surfaces of colloid particles suspended in a solution of the hydrolyte—not between substances in actual solution, as in the case of soluble acids and the soluble glucosides.

It was long customary to regard these two cases of change as similar in form and as mass-action effects. In the course of the extended inquiry into the action of urease on urea, by Armstrong and Horton† and by Armstrong, Benjamin and Horton,‡ however, results were brought to light which could not well be interpreted otherwise than on the assumption, first put forward by Duclaux, that the hydrolysis took place at a practically "linear rate" and that the approximately "logarithmic rates" observed in most cases of enzymic hydrolysis were the result of interferences with the "linear rate" due to the action of the products of change.

Careful experimental work showed, in fact, that enzymic changes would take place at apparently constant rates were it not that they are subject directly and indirectly to considerable retardation by the products of change. Urea, for example, is hydrolysed to carbonic acid and ammonia by urease; when the hydrolysis is effected in presence of an excess of either of these products, the rate is approximately a linear function of the time. Ammonia has a definite retarding influence on the enzyme; but if this effect be

\* 'Roy. Soc. Proc.,' B, vol. 86, pp. 561–586 (June, 1912).

† 'Roy. Soc. Proc.,' B, vol. 85, p. 109 (1912).

‡ 'Roy. Soc. Proc.,' B, vol. 86, p. 328 (1913).

neutralised by introducing an excess of carbonic acid—which presumably is too weak an acid to influence the enzyme—the change takes place much more rapidly than in the absence of the acid and practically at a linear rate.

On the other hand, hydrolysis conditioned by acids is a bimolecular process, effected by the breakdown of a system composed of the hydrolyte, the catalyst and water; as such it follows the laws of mass action, its rate being expressed by the well-known logarithmic law. Hence no analogy exists between the catalytic action of enzymes and of acids; indeed that of acids is not one in which surface phenomena and colloid structure are concerned.

In the case of the hydrogenation of oils, in presence of nickel, it is beyond question that the catalyst is active in the solid state; the fact, that, as will now be shown, action takes place in a manner which is clearly similar to that observed in the case of the hydrolysis of urea under the influence of urease, is the strongest possible argument in favour of the view put forward to explain the action of this enzyme and indeed of enzymes generally.

The catalytic hydrogenation of liquid fats in presence of nickel has been studied by measuring the volume of hydrogen entering and leaving the system. In our most recent experiments, this has been effected by water meters designed to measure 2.5 litres of gas per revolution; it was found that accurate results were obtainable when the gas entering each meter was brought to constant temperature by passage through metal coils immersed in the same water-bath. The meters were checked against each other before and after each experiment, to guard against constant errors due to the meters not recording with equal accuracy; they were also calibrated fairly frequently by passing a known volume (10 litres) of hydrogen through them.

The purest obtainable oils of a number of types were used, viz. :—

Oil.	Iod. No.	Composition (Lewkowitch, Oils, Fats and Waxes, 1914 Edition, vol. 2).
Olive .....	84.6	About 90 per cent. olein, 5 per cent. linolein, and 25 per cent. palmitin.
Cotton-seed .....	113.6	About 80 per cent. linolein, 25 per cent. olein, and 25 per cent. palmitin.
Whale .....	181.4	Glycerides of acids of varying degrees of unsaturation.
Linseed .....	184.6	A large proportion of linolenin and linolein, with about 20 per cent. olein and about 5 per cent. of saturated glycerides.

Very many experiments have been made, but it will be sufficient for the purpose of the present discussion to quote only the results of three.

(i) Cotton-seed Oil. 300 grm. oil; 0.3 per cent. Ni; 180° C.

Meter temperature.	Time.	dt.	Temperature.	Passed.	Gas volume.		dv.	dv/dt.
					Emerg.	Absorbed.		
° C.	mins.	—	° C.	litres.	—	—	—	—
26	0.00	—	175	0.00	—	—	—	—
	2.07	2.07	186	2.60	0.75	1.75	1.75	0.85
	4.08	1.96	182	5.00	1.36	3.64	1.89	0.97
	5.95	1.92	182	7.50	2.01	5.49	1.85	0.96
	7.98	2.03	181	10.00	2.56	7.44	1.95	0.96
	10.03	2.05	182	12.50	3.14	9.36	1.92	0.93
	12.07	2.04	181	15.00	3.75	11.25	1.89	0.93
	14.02	1.95	180	17.50	4.48	13.02	1.77	0.91
	16.05	2.03	179	20.00	5.43	14.57	1.55	0.77
	18.08	2.03	179	22.50	6.57	15.93	1.86	0.97
	20.13	2.05	181	25.00	7.85	17.35	1.42	0.69
	22.08	1.90	181	27.50	8.91	18.59	1.22	0.64
	24.06	0.92	180	30.00	10.09	19.91	1.32	0.65
	26.13	2.08	179	32.50	11.35	21.15	1.24	0.60
	28.07	1.94	179	35.00	12.05	22.35	1.20	0.62
	29.95	1.88	179	37.50	14.15	23.35	1.00	0.53
	31.95	2.00	179	40.00	15.57	24.43	1.08	0.54
	33.87	2.02	179	42.50	17.07	25.43	1.00	0.50
	36.08	2.06	179	45.00	18.57	26.43	1.00	0.49
	38.07	2.04	180	47.50	20.14	27.86	0.98	0.46
	40.10	2.08	179	50.00	21.80	28.20	0.84	0.41
27	42.17	2.07	179	52.50	23.50	29.00	0.80	0.39
	44.15	1.98	178	55.00	25.31	29.69	0.69	0.35
	46.22	2.07	180	57.50	27.17	30.33	0.66	0.32

(ii) Whale Oil. 150 grm. oil; 0.5 per cent. Ni; 180° C.

Meter temperature.	Time.	dt.	Temperature.	Passed.	Gas volume.		dv.	dv/dt.
					Emerg.	Absorbed.		
° C.	mins.	—	° C.	litres.	—	—	—	—
26	0.00	—	175	0.00	—	—	—	—
	1.35	1.35	180	2.50	1.09	1.41	1.41	1.05
	2.85	1.50	180	5.00	2.05	2.95	1.54	1.03
	4.28	1.43	179	7.50	3.16	4.34	1.89	0.97
	5.80	1.52	178	10.00	4.28	5.72	1.38	0.91
	7.32	1.52	178	12.50	5.47	7.08	1.81	0.86
	8.88	1.56	180	15.00	6.88	8.12	1.09	0.70
	10.88	1.50	182	17.50	8.30	9.14	1.02	0.68
	11.95	1.57	182	20.00	9.85	10.15	1.01	0.64
	13.40	1.45	182	22.50	11.37	11.13	0.98	0.67
	14.95	1.55	183	25.00	12.87	12.13	1.00	0.65
	16.48	1.53	184	27.50	14.44	13.06	0.98	0.61
	18.08	1.60	182	30.00	16.02	13.98	0.92	0.58
	21.35	3.27	178	35.00	19.40	15.60	1.12	0.50
	24.45	3.10	178	40.00	23.14	16.86	1.26	0.41
	27.37	2.92	180	45.00	27.20	17.80	0.94	0.32
	30.45	3.08	182	50.00	31.60	18.40	0.60	0.20

(iii) Linseed Oil. 150 grm. oil ; 0.2 per cent. Ni. ; 230° C.

Meter tempera- ture.	Time.	dt.	Tempera- ture.	Passed.	Gas volume.		d $\phi$	d $\phi$ /dt.
					Emerg.	Absorbed.		
° C.	mins.		° C.	litres.				
22½	0.00	—	225	0.00	—	—	—	—
	1.70	1.70	237	2.50	0.04	1.86	1.86	1.09
	3.83	2.13	230	5.00	1.00	3.91	2.05	0.96
	5.58	1.75	230	7.50	1.07	5.83	1.92	1.09
	7.53	1.95	231	10.00	2.14	7.86	2.03	1.04
	9.48	1.95	231	12.50	2.04	9.86	2.00	1.03
	11.45	1.97	231	15.00	3.85	11.65	1.79	0.91
	13.40	1.95	230	17.50	4.71	12.79	1.14	0.58
	15.38	1.98	228	20.00	6.56	13.44	0.65	0.30
	19.57	4.19	228	25.00	10.32	14.68	1.24	0.30
	23.43	3.86	231	30.00	14.25	15.75	1.07	0.27
	27.37	3.94	231	35.00	18.16	16.84	1.09	0.27
	31.50	4.13	229	40.00	22.08	17.92	1.08	0.26
	39.45	7.95	228	50.00	30.25	19.75	1.83	0.23
	47.52	8.07	230	60.00	38.67	21.33	1.58	0.20
	55.70	8.18	228	70.00	47.34	22.66	1.33	0.16

TYPICAL EXPERIMENTAL DATA

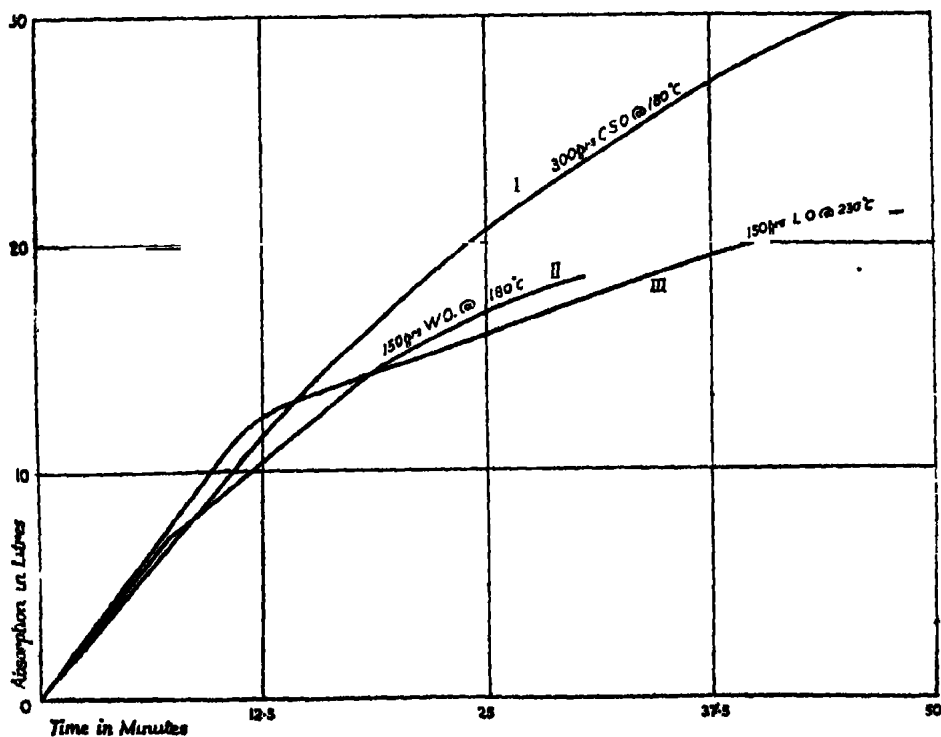


FIG 1

The data are reproduced in diagram 1. It is obvious that the curves (representing absorption of hydrogen plotted against time) show a general similarity.

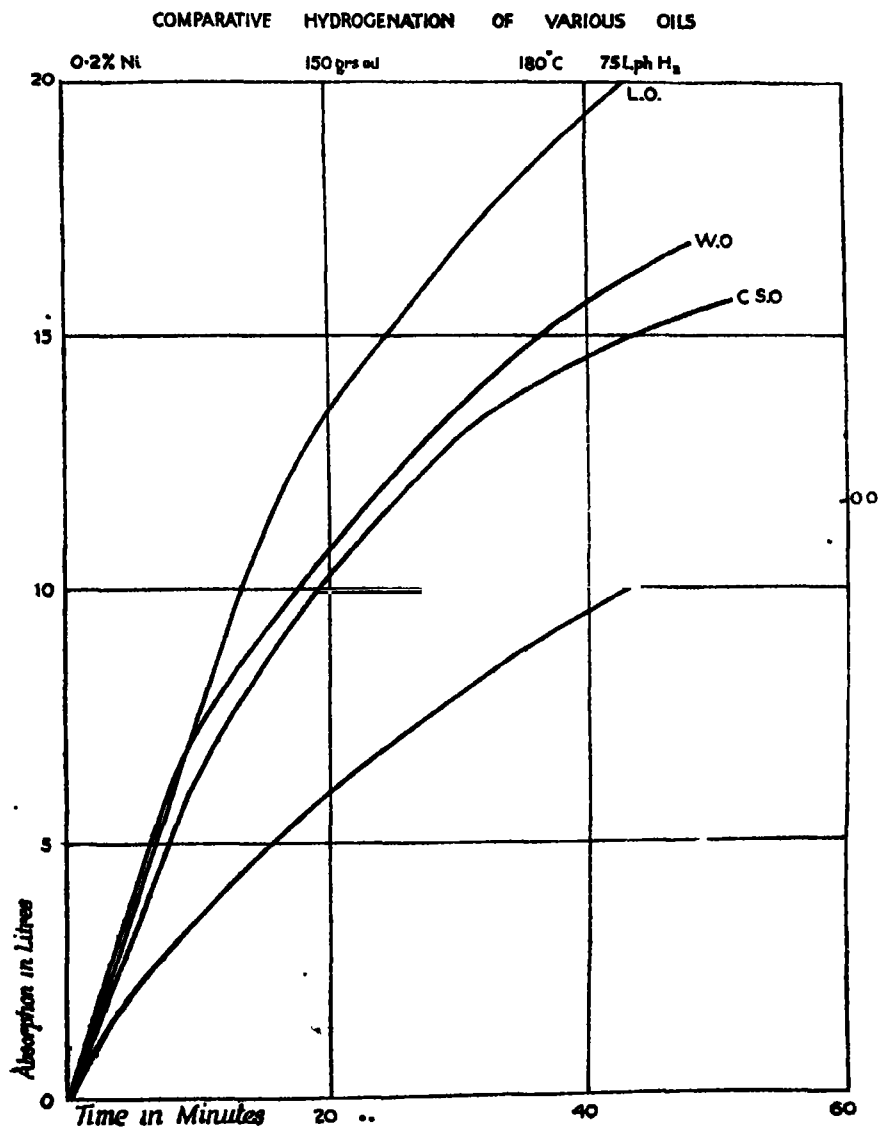


FIG. 2

Diagram 2 is a graph representing the course of hydrogenation of equal quantities (150 grm.) of linseed (L.O.), whale (W.O.), cotton-seed (C.S.O.) and olive (O.O.) oils.



All the curves, excepting those for olive oil, are characterised by an initial linear segment; this is followed by an abrupt change of direction to a segment of gentler slope, which is also linear at first but subsequently may exhibit considerable curvature.

The position of the point of inflexion on these curves merits some attention, as it takes place, approximately, at a corresponding part of each curve, at a point when, apparently, only 10–20 per cent. of the glycerides present is derived from acids less saturated than olein. This is clear when the rates of absorption of hydrogen (litres per minute) are compared for various portions of the curves:—

Oil.	To point of inflexion.	Succeeding			
		10 mins.	20 mins.	30 mins.	40 mins.
Olive . . . . .	0·45	0·28	0·24	0·17	0·14
Cotton-seed . . . . .	0·67	0·40	0·28	0·18	0·10
Whale . . . . .	0·74	0·36	0·26	0·21	0·14
Linseed . . . . .	0·72	0·34	0·27	0·24	—

Thus, in oils containing appreciable quantities of glycerides of acids more unsaturated than oleic, the rate of hydrogenation is the same as far as the point of inflexion; this point is, as it were, the pivot of the whole curve, since the succeeding rates, during the same time increments, are also approximately equal for each oil. The case of olive oil, which contains but little linolein, is complicated by the change of direction taking place almost immediately after the commencement of the action, so that the exact point of inflexion is very difficult to determine. Oils from various sources, consisting of mixtures of closely allied unsaturated glycerides, are hydrogenated, broadly speaking, at a constant rate until only about 10–20 per cent. of glycerides more unsaturated than olein is left, after which an abrupt change occurs. Soon, however, the rate settles down again to approximate constancy; then, after an interval, it gradually declines, as a state of saturation is approached. We have, therefore, to distinguish two well-defined linear components of the curves, namely, (1) the portion corresponding to glycerides more unsaturated than olein, (2) the part representing the hydrogenation of olein. In fact, the course of the change is to a great extent specific, that is to say, dependent on the nature of the unsaturated organic compound.

Turning to a more general interpretation of the curves, it is seen that these never approach the logarithmic type required for a unimolecular action, whilst they conform still less to those representative of bi- or ter-molecular

actions. On the other hand, over the greater portion of their course, they must represent, to comply with the law of mass action, the measurement of some change in which the acting mass is constant; it would therefore appear that either the rate of action of the catalyst or (possibly) that of the hydrogen is being portrayed, since these are the only substances present whose concentration can remain unchanged.

Further consideration of the above data have led us to the opinion, (i) that the agent in question is the catalyst; (ii) that the process of catalytic hydrogenation, in the solid liquid state, involves the primary formation of an unstable complex or "intermediate compound" between nickel and the unsaturated organic compound; the following is a necessarily condensed outline of the reasoning we have adopted:—

If the acting mass measured be *hydrogen*, the following changes are possible:—

(i) *Direct Interaction of Hydrogen and Fat at the Unsaturated Linkage.*

This case is excluded, as, on the one hand, such an action is infinitely slow, except in presence of a catalyst; whilst, on the other hand, if we assume that the catalyst does not play a chemical part but merely acts in virtue of some physical peculiarity of its surface, the interaction should follow either a "unimolecular" or a "bimolecular" course.

(ii) *Primary Formation of a Nickel-Hydrogen Complex, followed by Interaction of the Latter and the Unsaturated Organic Compound.*

In this case, if the speed of each component action be of the same order, the absorption-time-curves cannot be linear, since the rate of interaction of the nickel-hydrogen complex and the unsaturated compound must affect the equilibrium of the first action.

If the rate of the second action be so great that the absorption measured is only an indication of the speed of formation of the supposed complex, the latter, being independent of any factors but nickel and hydrogen, should lead to identical absorption-time-curves throughout; moreover, in particular, the well-marked point of inflexion on the curve (corresponding directly to a definite phase in the composition of the partly saturated glycerides) would be quite out of the question. Accordingly, this explanation is in direct conflict with observed facts.

If, conversely, the rate of the second interaction be much slower than that of the first and is thus the actual chemical change that is being measured, then, unless the concentration of the nickel-hydrogen complex be throughout very much greater than the "concentration of the unsaturated complex" (which is improbable, if only by reason of the small proportion of nickel

present), the effect of the latter, which is of course rapidly decreasing, must make itself felt so that the resulting action will appear to be either uni-molecular or bimolecular.

If the acting mass measured be *nickel*, we may have

(ii) *Primary Formation of a Nickel-Hydrogen Complex, etc., as dealt with in the preceding; or*

(iii) *Primary Interaction of Nickel and Fat at the Unsaturated Linkage followed by Further Action of Hydrogen on the Unstable System so Produced and the Formation of a Saturated Fatty Compound and Regenerated Nickel.*

Here, again, if the experimental data were a measure of the first phase of the change, it is difficult to see how linear graphs could result, bearing in mind the diminishing concentration of the unsaturated constituent. If, however, the formation of the assumed complex ( $\text{Ni lead} - \text{CH}:\text{CH}-$ ) were a preponderatingly fast equilibrium interaction with the balance strongly in favour of the unassociated constituents, it is possible that any variation in the speed of formation of the complex would be negligible in comparison with the slower rate of the second (measured) action; at the same time, it is also possible that the various complexes formed by nickel with the different unsaturated glycerides present would be acted on by hydrogen at varying rates, thus allowing for linear segments of varying slope.

We have observed that, when hydrogen containing small quantities of carbon monoxide is used to hydrogenate oil, the emerging gas is deprived of the carbon monoxide but contains, as near as we can ascertain, an equivalent quantity of methane; in other words, the carbon monoxide has been hydrogenated during its passage through the oil:—

Temperature of experiment.	Per cent CO (original).	Per cent. CO in emerging gas (corrected for contraction).	Per cent. $\text{CH}_4$ in emerging gas (these figures are only approximate).
° C.			
200	2.0	1.6	0.6—1.0
200	0.25	0.25	0.8—0.7
200	Nil	Nil	Nil

In this case, two gases, one of them present in very small concentration, are caused to interact by the solid metal surrounded with oil. Moreover, the amount of change effected is as much, if not more, than the amount which takes place under similar conditions in absence of oil. Sabatier\*

\* 'La Catalyse en Chimie Organique,' p. 66.

states that carbon monoxide and hydrogen commence to interact, forming methane and water, in presence of finely-divided nickel, at about  $190^{\circ}\text{C}$ ., the action becoming rapid only at and above  $230^{\circ}$ – $250^{\circ}\text{C}$ .; we have confirmed this statement. In the case of the hydrogenation of vapours of unsaturated substances, Sabatier\* has also emphasised the fact that the action is absolutely inhibited by any film of liquid condensed on the nickel.

We therefore consider that it is possible that a small quantity of nickel carbonyl is formed and that this, in solution in the oil, is decomposed by the hydrogen, forming methane, water and nickel; again, therefore, we have combination between nickel and an unsaturated compound preceding hydrogenation of the latter.

We may cite here a further fact which, in common with the well-marked character of the "linolein" and "olein" linear segments of the preceding curves, indicates the dependence of catalytic hydrogenation on the specific type of the unsaturated organic compound: the optimum temperature of hydrogenation is not the same for all compounds in presence of nickel, as might be expected if the catalysis depended merely on the presentation under certain special conditions of hydrogen by the catalyst to the organic compound. Thus, whilst the simpler olefines and acetylene, according to Sabatier, are most smoothly hydrogenated to the corresponding paraffins at about  $150^{\circ}\text{C}$ ., the hydrogenation of unsaturated glycerides and of the benzenoid nucleus proceeds best at  $170^{\circ}$ – $180^{\circ}\text{C}$ .; again the reduction of carbon monoxide to methane does not proceed rapidly till about  $230^{\circ}$ – $250^{\circ}\text{C}$ . It is interesting, in this connection, that copper, which does not form a copper carbonyl derivative, is unable to effect the hydrogenation of carbon monoxide, although it is active in converting many olefines into paraffins in presence of hydrogen.

An instance has been given by Schlenck (D.R.P. 292310) of a definite metallic compound of sodium with an ethylenic linkage, which is comparable with that of an unstable nickel-unsaturated-organic-compound-complex which we have outlined above. Stilbene, when treated in solution in an inert medium with finely-divided sodium, in absence of oxygen, water or carbon dioxide, was observed to give a compound  $\text{C}_6\text{H}_5\text{CHNa}\cdot\text{CHNa}\cdot\text{C}_6\text{H}_5$ , which by treatment with water gave sym.-diphenylethane,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , and sodium hydroxide.

The general aspect of the curves obtained for catalytic hydrogenation is markedly similar to those obtained in the case of enzymes and they undoubtedly represent related phenomena. In each case, the catalyst (enzyme or reduced nickel) unites primarily with the organic compound about

\* *Ibid.*, p. 56.

to undergo change (hydrolyte or unsaturated glyceride), the complex so formed being decomposed by the other component of the interaction (water or hydrogen). In each case, moreover, action takes place entirely at the surface of minute particles and the activity of the catalyst depends entirely on the production of the maximum surface and the avoidance of impurities likely to destroy or dirty this surface.

In attempting to explain the nature of the influence of the nickel catalyst in promoting the hydrogenation of fatty oils, we see no reason to depart from the view laid down in the discussion of enzyme action referred to, that the interchanges take place in an electrolytic circuit in which the interacting substances are necessarily all comprised. The hydrogen and the fatty oil are both to be thought of as coupled with the nickel and the interaction as brought about through the inclusion in the system of the electrolyte required to establish a conducting circuit. Both hydrogen and the fatty oil are to be regarded as having some affinity for the catalyst; and the rate of change is to be considered as determined by the rate at which the less active (hydrogen) enters into productive association with the catalyst. A gradual falling-off in the rate of change is to be anticipated—greater probably than that observed in aqueous solutions—owing to the slowness with which diffusion would take place in the oily medium and the consequent growth of mechanical interference due to the diminution of the amount of the unsaturated compounds and increase of the saturated; also, it is to be supposed that the specific attractive influence of the nickel for the unsaturated organic compound would diminish as the degree of unsaturation of the oils were lowered, as indeed is definitely indicated by our experimental results.

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*The Value of the Rydberg Constant for Spectral Series.*

By W. E. CURTIS, B.Sc., Demonstrator of Astrophysics at the Imperial College of Science, South Kensington.

(Communicated by Prof. A. Fowler, F.R.S. Received April 9, 1919.)

*Introductory.*

In a previous paper,\* the results of a series of measurements of the wave-lengths of the first six lines of the Balmer series of hydrogen were given, together with a determination of the Rydberg constant for spectral series. It has recently been pointed out to me by Prof. Fowler that the value of the series constant there obtained is not quite correct, in consequence of errors in the corrections applied to the observed wave-lengths to reduce them to *vacuo*, the data employed for this purpose having been taken from a Table† appropriate to wave-lengths in air at 20° C., whereas the tertiary standards of iron upon which the wave-length determinations were based referred to 15° C. Before the introduction of the International system, wave-lengths had always been given for air at 20° C., and there was no explicit mention of the change of standard temperature in the paper‡ by Burns, from which the iron arc wave-lengths used as standards were taken. The oversight might possibly have been detected earlier but for the author's absence on military service from September, 1914, to January, 1919. In any case, however, a revision of the previous work would have been necessary in view of the recent accurate determinations at the Bureau of Standards of the refractive index of air,§ and also of other work, both theoretical and experimental, on the Balmer series, which has been carried out since 1914.

The correction in question is of the order of +0.02 Å, and results, as will be seen, in a decrease of nearly one unit in the value of the Rydberg constant.

*Corrected Wave-lengths and Wave-numbers.*

The corrected values of the wave-lengths (*in vacuo*) and wave-numbers are tabulated below. The last column gives the values of  $N$  derived from each line by applying the Balmer formula. Although the observed wave-lengths in air are only recorded to the third place of decimals, it is advisable to take

\* 'Roy. Soc. Proc.,' A, vol. 90, p. 605 (1914).

† Kayser, 'Spectroscopie,' vol. 2, p. 514.

‡ 'Lick Obs. Bull,' vol. 8, No. 247 (1913).

§ Bureau of Standards, Washington, 'Scientific Papers,' No. 327 (1918).

out the corrections to the fourth place, in order to prevent the possibility of accumulated error affecting the third figure.

Table I.

$m$ .	$\lambda$ air.	Correction.	$\lambda$ vac.	$\nu$ vac.	$\frac{4m^2\nu}{m^2-4}$ .
3	6562.793 I.A.	+1.8092	6564.6022	15233.216	109679.155
4	4861.326	+1.3537	4862.6797	20564.793	109678.896
5	4340.467	+1.2160	4341.6830	28032.543	109678.776
6	4101.788	+1.1535	4102.9315	24378.055	109678.748
7	3970.075	+1.1190	3971.1940	25181.843	109678.788
8	3889.051	+1.0979	3890.1469	25705.957	109678.750

The systematic variation of  $N$ , of magnitude exceeding that which could be attributed to experimental error, indicates, as was previously found to be the case, that the Balmer formula is only an approximation to the truth.

*Discussion of Formulæ Investigated.*

The formulæ examined may all be written in the form

$$\nu = N \left( \frac{1}{4} - \frac{1}{m^2} \right) + f(m, N).$$

Since Balmer's law is so nearly exact,  $f(m, N)$  is of the nature of a small correction to  $N \left( \frac{1}{4} - \frac{1}{m^2} \right)$ , never exceeding 0.002 per cent. of the latter quantity in any of the formulæ under discussion. The exact form of this function, however, exercises an important influence on the value obtained for  $N$ .

It is natural to try first a formula of the Rydberg type, viz. :—

$$\nu = \frac{N}{(2+p)^2} - \frac{N}{(m+\mu)^2}. \quad (I)$$

The most convenient method of solution is to assume an approximate value,  $N'$ , such that the true value  $N = N' + \delta N$ . Then, neglecting the second and higher powers of  $p$  and  $\mu$ , we obtain

$$\delta N + \frac{8\mu N'}{m(m^2-4)} - \frac{N'pm^2}{m^2-4} = \frac{4m^2\nu}{m^2-4} - N'.$$

A least-squares solution gives

$$N = 109678.278, \quad \mu = +0.0210, \quad p = -0.0383.$$

This, as will be seen from Table II, represents the results satisfactorily, but, before adopting this formula, it is necessary to examine whether an equally good representation of the series can be obtained by employing only two constants.

Retaining  $\mu$  and  $N$ , the formula becomes

$$\nu = \frac{N}{4} - \frac{N}{(m + \mu)^2}. \quad (\text{II})$$

The least-square values are

$$N = 109678.725, \quad \mu = +0.074.$$

The observed *minus* calculated values suggest a slight inferiority to formula (I), but not more than would be expected in view of the elimination of one constant. Since the representation is within the limits of probable experimental error, one must conclude that the introduction of the third constant is not justifiable.

Retaining  $p$  instead of  $\mu$ , the formula becomes

$$\nu = \frac{N}{(2 + p)} - \frac{N}{m^2}. \quad (\text{III})$$

A least-square solution gives

$$N = 109678.10, \quad p = -0.053.$$

This again appears to be quite satisfactory as regards the numerical agreement with the observed wave-lengths. The superiority over (II), however, is too slight to warrant the definite adoption of (III) in preference to (II), but the conclusion is confirmed that the present data do not necessitate a formula including more than two constants.

Turning now to theoretical investigations in connection with the radiation of the hydrogen atom, Dr. Bohr has modified his well-known derivation of the Balmer formula by introducing a small correction due to the dependence of the mass of the electron upon its velocity.\* He thus obtains the formula

$$\nu = N \left( \frac{1}{4} - \frac{1}{m^2} \right) \left\{ 1 + k \left( \frac{1}{4} + \frac{1}{m^2} \right) \right\}. \quad (\text{IV})$$

Applying this to the observed wave-numbers, the method of least-squares gives

$$N = 109677.58, \quad k = +0.387.$$

It will be seen from Table II that this formula is inferior to either (II) or (III), both of which employ the same number of constants, namely, two. The 0 *minus* C residuals exceed the probable error of the wave-length determination in two cases, viz., H $\gamma$  and H $\zeta$ , the former being the best determined line of the six. Moreover, the deviation tends to be systematic, a feature which is brought out very distinctly by calculating the constants from two lines instead of by the method of least-squares.

\* 'Phil. Mag.,' vol. 29, p. 332 (1915).



The theoretical expression for  $k$  is  $\pi^2 e^4 / c^2 h^2$ , where

$e$  = charge of electron,

$c$  = velocity of light,

$h$  = Planck's element of action.

This, when evaluated, gives  $k = +0.04133$ , about one-third of the value found above. The sign and order of magnitude are certainly right, and the discrepancy is possibly no more than could be attributed to error arising from the compound nature of the lines, a point which is considered in the succeeding section.

Dr. Allen, by taking account of the magnetic moment of the atomic nucleus, has obtained an expression of the form

$$\nu = \frac{N}{4} - \frac{N}{\left(m + \frac{B}{m^2}\right)^2}. \quad (\text{V})$$

The least-square values derived from this formula are

$$N = 109678.76, \quad B = +0.04629.$$

It is singular that the value of  $B$  should agree precisely with that obtained by Allen on the assumption of five magnetons, but the exactness of the agreement can only be accidental. Moreover, the residual for  $H\beta$  is distinctly too large to permit us to regard this type of formula as satisfactory. In fact, neither this nor formula (IV) seems to be of a quite suitable shape to represent the observed values. It is considered that these latter are hardly likely to be in error by more than the amounts shown in the third column of Table II, in view of the fact that the Rydberg type of formula gives such good results.

The formula originally proposed by Dr. Allen was more general than the above, and was of the form

$$\nu = \frac{N}{\left(2 + \frac{B}{4}\right)^2} - \frac{N}{\left(m + \frac{B}{m^2}\right)^2}. \quad (\text{VI})$$

With this type of formula,  $B$  is necessarily negative, but there would seem to be no objection to this on theoretical grounds. A least-square solution gives

$$N = 109677.79, \quad B = -0.03144.$$

The representation is much better than in the case of V, the residuals being comparatively small, but they exhibit a distinct tendency towards systematic variation, so that the formula cannot be considered so good as any of the Rydberg forms. It may be noted, however, that the above value of  $B$  is

exactly that obtained theoretically on the assumption of three magnetons in the core of the atom.

One other type of formula has been examined, and the results are perhaps worth recording, although it does not give a quite satisfactory fit, nor has it any theoretical basis so far as is known. The only point of interest in connection with it is that only one constant is employed. If we write  $1/N$  for  $\mu$  in formula (II) we get

$$\nu = \frac{N}{4} - \frac{N}{\left(m + \frac{1}{N}\right)^2}. \quad (\text{VII})$$

The average value of  $N$  is 109678.70, and the only sensible residual is that corresponding to  $H\alpha$ , which, however, is too large to be admissible.

Table II.—Comparison of Formulæ.

m.	$\lambda$ obs. (air).	Probable error $\times 10^4$ .	( $\lambda$ obs. — $\lambda$ calc.) $\times 10^4$ .						
			(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
3	6562.798 I.A.	$\pm 17$	+2	+2	-2	-11	+6	-6	-47
4	4861.326	10	-9	-16	-6	+5	-30	+5	+9
5	4840.487	6	+8	+4	+8	+15	0	+13	0
6	4101.738	13	+5	+3	+3	+5	+7	+5	-3
7	3970.075	16	-1	+1	-2	-4	+7	-4	+5
8	3889.061	11	-7	-4	-9	-15	+3	-18	+11
$\Sigma \Delta$			-2	-10	-8	-5	-7	0	-25
$\Sigma \Delta^2$			224	302	198	687	1043	440	2445

*Effect of Composite Structure of Lines.*

Before attempting to decide upon the best value to adopt for  $N$ , in view of the foregoing discussion of formulæ, it is necessary to take account of the structure of the lines. It has long been known that at least two components existed in the case of  $H\alpha$  and  $H\beta$ , and presumably this complexity exists also in the other members. Obviously, then, for the complete representation of the series as many formulæ as there are components will be required, and the value of  $N$  derived from measurements of the unresolved lines (as they were in the present case) will not necessarily be the true one. If the intensity distribution were very unsymmetrical an appreciable error might be introduced in this way. An attempt has been made to estimate the amount of the uncertainty due to this cause, but it is difficult to do so with any degree of exactitude. In the first place, the precise structure would still appear to be in some doubt. Bohr mentions "the fact that the hydrogen

lines, when observed by instruments of high dispersive power, are split up in a number of components situated close to each other," but the reference is not given, and has not yet been traced.

According to the observations of Merton and Nicholson,\*  $H\alpha$  and  $H\beta$  are doublets, the separations (0.132 and 0.030 respectively) corresponding to a principal type of series. They agree with previous investigators that the ratio of intensities is about 10 : 7, the less refrangible component being the stronger. If it be assumed that the wave-length determinations really refer to the "optical centre of gravity," *i.e.*, a point  $7/17$  of the separation from the less refrangible component, and if it be further supposed that the series is of the principal type, it is possible to calculate the wave-lengths of the individual components. The former assumption would hardly be permissible if their actual wave-lengths were required, but the object here is merely to estimate to what extent the duplicity of the lines may affect the value of  $N$ .

If we adopt formulæ of type II we shall have

$$\nu' = \frac{N}{4} - \frac{N}{(m + \mu')^2}, \quad \nu'' = \frac{N}{4} - \frac{N}{(m + \mu'')^2}$$

The wave-number interval,

$$d\nu = \nu' - \nu'' = \frac{N}{(m + \mu'')^2} - \frac{N}{(m + \mu')^2} = \frac{2(\mu' - \mu'')N}{m^3}, \text{ approx.,}$$

and the wave-length interval

$$d\lambda = -\frac{\lambda}{\nu} d\nu = \frac{2\lambda(\mu'' - \mu')N}{\nu m^3} = \frac{32 \times 10^8 (\mu'' - \mu')}{N} \times \frac{m}{(m^2 - 4)^2},$$

or  $d\lambda = \frac{km}{(m^2 - 4)^2}$ , where  $k$  is a constant which can best be determined from the separation of  $H\alpha$ .

Assuming for this the value 0.132, the separations of  $H\beta$ , etc., come out 0.031, 0.012, 0.007, 0.004, and 0.002 respectively.

Table III.

Less refrangible components.		More refrangible components.	
Assumed $\lambda$ (air).	0—C.	Assumed $\lambda$ (air).	0—C.
6562.847 I.A.	+0.000	6562.716 I.A.	+0.000
4861.839	-0.001	4861.808	-0.001
4840.472	+0.001	4840.460	+0.001
4101.741	+0.000	4101.784	+0.001
3970.077	+0.000	3970.078	+0.000
3889.052	-0.000	3889.050	-0.000

\* 'Phil. Trans.,' A, vol. 227, p. 227 (1917).

By applying the first assumption the wave-lengths given in Table III were obtained. The calculation of formulæ of type (II) for these gave  $N = 109678.73$ ,  $\mu' = -0.082$ ,  $\mu'' = +0.030$ .

As will be seen, the fit is satisfactory in both cases, and there is no appreciable change in the value of  $N$ . If instead of formula (II), either (I) or (III) be used, a similar result follows, that is to say, the values of  $N$  respectively obtained differ but little from those already given. So that if the doublets are really of principal type, or, more generally, if they show a rapid decrease of wave-number interval as  $m$  increases, the consequent uncertainty in the value of  $N$  is not serious.

If instead of dealing with the "optical centre of gravity" it be supposed that the settings were made midway between the edges of the lines (and this is certainly what was attempted), the values of  $\mu$  become  $-0.0412$  and  $+0.0427$ , and again there is no appreciable change in the value of  $N$ .

On the other hand, the values obtained for  $\mu$  are considerably affected by the question of the structure of the lines, and cannot be determined with any degree of accuracy from measurements on unresolved doublets. Two interesting possibilities present themselves, however, and may be noticed here. One is that the Balmer law may hold rigorously for one of the components of each line. The fact that the  $\mu$  of formula (II) comes out positive excludes this possibility as far as the more refrangible component is concerned, and a simple calculation shows that for the less refrangible component,  $\mu$  could only be zero if the settings had been made on a point situated about one-fifth of the separation ( $0.132$ ) from the latter component. This would appear to require a much larger difference of intensity than has been found experimentally, so that in all probability neither component is exactly represented by the Balmer formula.

The second possibility in question is that the components of each line may be symmetrically situated on either side of the positions indicated by Balmer's law. If this were so,  $\mu'$  and  $\mu''$  would be equal and of opposite signs, and it is found that the measurements would have to be taken as referring to a point five-sevenths of the separation from the less refrangible component. This would only be the case if the more refrangible were the stronger, which is again in disagreement with the experimental evidence.

#### *The Value of the Series Constant.*

From the preceding remarks, it will be seen that the chief difficulty in determining the most probable value of  $N$  arises not so much from the non-homogeneity of the lines as from the uncertainty as to the proper type of

formula to be adopted. The results given by the various formulæ are summarised below :—

$$\begin{aligned}
 \text{(I.)} \quad \nu &= \frac{N}{(2+p)^2} - \frac{N}{(m+\mu)^2}, & N &= 109678.28. \\
 \text{(II.)} \quad \nu &= \frac{N}{4} - \frac{N}{(m+\mu)^2}, & N &= 109678.73. \\
 \text{(III.)} \quad \nu &= \frac{N}{(2+p)^2} - \frac{N}{m^2}, & N &= 109678.10. \\
 \text{(IV.)} \quad \nu &= N \left( \frac{1}{4} - \frac{1}{m^2} \right) \left\{ 1 + k \left( \frac{1}{4} + \frac{1}{m^2} \right) \right\}, & N &= 109677.58. \\
 \text{(V.)} \quad \nu &= \frac{N}{4} - \frac{N}{\left( m + \frac{B}{m^2} \right)^2}, & N &= 109678.76. \\
 \text{(VI.)} \quad \nu &= \frac{N}{\left( 2 + \frac{B}{4} \right)^2} - \frac{N}{\left( m + \frac{B}{m^2} \right)^2}, & N &= 109677.79.
 \end{aligned}$$

It will be observed that the two theoretical formulæ (IV) and (VI) give the lowest values, but neither can be regarded as definitely supported by the experimental results. From the latter point of view, (I), (II), and (III) are all satisfactory and about equally good. For the present, until accurate determinations of the wave-lengths of the components (particularly of  $H\alpha$ ) become available, the adoption of 109678.3 as a provisional value is suggested. This is in agreement with that derived from (I), and is roughly intermediate between (II) and (III).

The amount of the uncertainty, about 0.5 at most, is probably not of serious consequence, having regard to the degree of accuracy of our present data in the case of most of the series lines of other elements. The same is true with reference to the correction (−0.9) now applied to the value (109679.2) given in the previous paper. Thus, for example, the conclusion of Nicholson,\* that the Rydberg constant derived from the Balmer series is also applicable to the helium series, does not require modification on this account.

The wave-lengths of all the lines down to  $m = 37$  have been recalculated in the hope that they may possibly prove of service in certain cases, such as, for example, the reduction of eclipse spectra, particularly those obtained with slitless spectrographs. Formula (I) was used for the purpose, and the differences from the previous values are extremely small, never more than 0.001 Å, in fact. The new values are given in Table IV below :—

\* 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

Table IV.—Wave-lengths (in Air) of Balmer Series Lines calculated by Formula (I).

m.	$\lambda$ (I.A.).	m.	$\lambda$ (I.A.).	m.	$\lambda$ (I.A.).
3	6562.798	15	3711.973	27	3606.097
4	4861.327	16	3708.855	28	3604.679
5	4340.468	17	3697.154	29	3603.405
6	4101.738	18	3691.557	30	3602.258
7	3970.075	19	3686.834	31	3601.221
8	3889.052	20	3682.810	32	3600.280
9	3835.387	21	3679.255	33	3599.423
10	3797.900	22	3676.265	34	3598.641
11	3770.633	23	3673.761	35	3597.926
12	3750.154	24	3671.478	36	3597.269
13	3734.371	25	3669.466	37	3596.666
14	3721.941	26	3667.684	$\infty$	3645.981

The above formula gives the convergence wave-number *in vacuo* as 27419.674, corresponding to a wave-length in air of 3645.981 I.A., which is exactly the same as that obtained in the previous paper.

#### Summary.

(1) The results given in a previous paper have been modified on account of a slight alteration now found to be necessary in the values of the corrections to vacuum.

(2) A number of formulæ, empirical and theoretical, have been compared, and it is found that a two-constant Rydberg formula is capable of representing the series satisfactorily, and shows an appreciable superiority in this respect over the theoretical formulæ of both Bohr and Allen.

(3) The probable effect upon the determination of  $N$  arising from the composite structure of the lines is investigated, and found to be inappreciable, except in so far as this non-homogeneity renders it somewhat uncertain which type of formula should be employed to represent the observed wave-lengths.

(4) The provisional adoption of the value 109678.3 for  $N$  is suggested. This is probably sufficiently accurate for present purposes, but could be improved upon if accurate wave-lengths of the individual components of  $H\alpha$  and  $H\beta$  were available.

(5) The calculated wave-lengths of the members of the series down to  $m = 37$  are given. These do not differ by more than 0.001 Å from the corresponding values given previously.

*Monoclinic Double Selenates of the Cobalt Group.*

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(Received May 9, 1919.)

This memoir deals with the four double selenates of the series  $R_2M(SeO_4)_2 \cdot 6H_2O$ , in which M is cobalt and R is potassium, rubidium, caesium, and ammonium. Only the potassium and ammonium salts of this cobalt group have been hitherto investigated. They were prepared and analysed by von Hauer,\* the crystals measured by Haldor Topsøe,† and their optical properties partially determined by Topsøe and Christiansen.‡ The salts were prepared for this present investigation by dissolving pure cobalt carbonate in the calculated quantity of dilute selenic acid, boiling off carbon dioxide, and filtering; then adding the solution of cobalt selenate so obtained to a molecularly equivalent quantity of a solution of the alkali selenate, one drop excess of selenic acid being eventually added to the mixed solution to ensure perfect clarity. The ammonium and potassium selenates were from a very pure stock prepared in some quantity a short time ago; the rubidium and caesium selenates were freshly prepared by dissolving the pure carbonates in selenic acid, and boiling off carbon dioxide. The crystallisations were effected from metastable solutions, with all the precautions previously described, and numerous crops of the beautiful ruby red crystals of all four salts were obtained, of which several in each case proved suitable for the measurements and determinations.

The work on these four salts is especially similar and parallel to that on the four analogous nickel salts described in 1916,§ so that descriptions of methods need not be again given, but merely the results communicated.

*Potassium Cobalt Selenate,  $K_2Co(SeO_4)_2 \cdot 6H_2O$ .*

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Axial Angle.*— $\beta = 104^\circ 17'$ . Topsøe's value  $104^\circ 10'$ .

*Ratio of Axes.*— $a : b : c = 0.7522 : 1 : 0.5062$ .

Topsøe's value  $0.7379 : 1 : 0.5056$ .

*Forms observed.*— $a\{100\}$ ,  $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $p'\{120\}$ ,  $q\{011\}$ ,  $\{201\}$ . The forms  $a$  and  $p'$  were not observed by Topsøe.

\* 'Wien. Akad. Sitzber.,' vol. 39, p. 839 (1869).

† 'Krytallogr.-kem. Unders. o. de Selenure Salte,' Copenhagen, 1870.

‡ 'Ann. de Chim. et de Phys.,' Ser. 5, vol. 1, pp. 78 and 79 (1874).

§ 'Phil. Trans. A,' vol. 217, p. 199 (1917).

## Interfacial Angles of Potassium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topog.
$ac = (100) : (001) \dots$	3	$75^{\circ} 45' - 75^{\circ} 51'$	$75^{\circ} 47'$	$75^{\circ} 43'$	4	'
$as = (100) : (101) \dots$	—	—	—	$46^{\circ} 27'$	—	—
$so = (101) : (001) \dots$	—	—	—	$29^{\circ} 16'$	—	—
$os' = (001) : (201) \dots$	12	$62^{\circ} 53' - 63^{\circ} 14'$	$63^{\circ} 7'$	$62^{\circ} 58'$	0	63 21
$os' = (001) : (101) \dots$	—	—	—	$38^{\circ} 6'$	—	—
$s'r' = (101) : (201) \dots$	—	—	—	$24^{\circ} 52'$	—	—
$r'a = (201) : (100) \dots$	2	$41^{\circ} 8' - 41^{\circ} 10'$	$41^{\circ} 9'$	$41^{\circ} 19'$	10	—
$r'e = (201) : (001) \dots$	14	$116^{\circ} 39' - 117^{\circ} 37'$	$116^{\circ} 52'$	$117^{\circ} 2'$	10	117 3
$ap = (100) : (110) \dots$	6	$35^{\circ} 51' - 36^{\circ} 6'$	$36^{\circ} 0'$	$36^{\circ} 3'$	3	—
$pp' = (110) : (120) \dots$	1	—	$19^{\circ} 25'$	$19^{\circ} 28'$	3	—
$p'b = (120) : (010) \dots$	—	—	—	$34^{\circ} 29'$	—	—
$pp'' = (110) : (130) \dots$	—	—	—	$29^{\circ} 21'$	—	—
$p''b = (130) : (010) \dots$	—	—	—	$24^{\circ} 36'$	—	—
$pb = (110) : (010) \dots$	2	$53^{\circ} 47' - 54^{\circ} 3'$	$53^{\circ} 55'$	$53^{\circ} 57'$	2	—
$pp = (110) : (110) \dots$	21	$71^{\circ} 50' - 72^{\circ} 21'$	$72^{\circ} 7'$	*	—	71 10
$pp = (110) : (110) \dots$	20	$107^{\circ} 38' - 108^{\circ} 1'$	$107^{\circ} 52'$	$107^{\circ} 53'$	1	108 43
$eq = (001) : (011) \dots$	39	$25^{\circ} 56' - 26^{\circ} 14'$	$26^{\circ} 8'$	*	—	26 7
$qb = (011) : (010) \dots$	6	$63^{\circ} 36' - 64^{\circ} 1'$	$63^{\circ} 48'$	$63^{\circ} 52'$	4	—
$qq = (011) : (011) \dots$	19	$127^{\circ} 35' - 127^{\circ} 55'$	$127^{\circ} 45'$	$127^{\circ} 44'$	1	—
$ao = (100) : (111) \dots$	—	—	—	$40^{\circ} 42'$	—	—
$aq = (111) : (011) \dots$	—	—	—	$27^{\circ} 31'$	—	—
$ao = (100) : (011) \dots$	—	—	—	$77^{\circ} 13'$	—	—
$qo' = (011) : (111) \dots$	—	—	—	$34^{\circ} 15'$	—	—
$o'a = (111) : (100) \dots$	—	—	—	$68^{\circ} 32'$	—	—
$oo = (001) : (111) \dots$	—	—	—	$35^{\circ} 1'$	—	—
$op = (111) : (110) \dots$	—	—	—	$43^{\circ} 29'$	—	—
$cp = (001) : (110) \dots$	40	$78^{\circ} 21' - 78^{\circ} 41'$	$78^{\circ} 30'$	*	—	78 21
$po' = (110) : (111) \dots$	—	—	—	$57^{\circ} 6'$	—	—
$o'o = (111) : (001) \dots$	—	—	—	$44^{\circ} 24'$	—	—
$pc = (110) : (001) \dots$	40	$101^{\circ} 16' - 101^{\circ} 38'$	$101^{\circ} 29'$	$101^{\circ} 30'$	1	101 29
$bn = (010) : (121) \dots$	—	—	—	$53^{\circ} 44'$	—	—
$no = (121) : (111) \dots$	—	—	—	$16^{\circ} 7'$	—	—
$bo = (010) : (111) \dots$	—	—	—	$69^{\circ} 51'$	—	—
$os = (111) : (101) \dots$	—	—	—	$20^{\circ} 9'$	—	—
$bo' = (010) : (111) \dots$	—	—	—	$65^{\circ} 9'$	—	—
$o'd = (111) : (101) \dots$	—	—	—	$24^{\circ} 51'$	—	—
$o'o' = (111) : (111) \dots$	—	—	—	$40^{\circ} 42'$	—	—
$eq = (101) : (011) \dots$	—	—	—	$38^{\circ} 27'$	—	—
$qp = (011) : (110) \dots$	36	$85^{\circ} 11' - 85^{\circ} 39'$	$85^{\circ} 25'$	$85^{\circ} 24'$	2	85 33
$ps = (110) : (101) \dots$	—	—	—	$56^{\circ} 9'$	—	—
$pq = (110) : (011) \dots$	36	$94^{\circ} 15' - 94^{\circ} 52'$	$94^{\circ} 33'$	$94^{\circ} 36'$	2	—
$s'q = (101) : (011) \dots$	—	—	—	$45^{\circ} 3'$	—	—
$qs = (011) : (121) \dots$	—	—	—	$26^{\circ} 52'$	—	—
$sp = (121) : (110) \dots$	—	—	—	$37^{\circ} 8'$	—	—
$qp = (011) : (110) \dots$	38	$63^{\circ} 47' - 64^{\circ} 17'$	$64^{\circ} 3'$	$64^{\circ} 0'$	3	64 16
$ps' = (110) : (101) \dots$	—	—	—	$70^{\circ} 57'$	—	—
$pq = (110) : (011) \dots$	38	$115^{\circ} 42' - 116^{\circ} 13'$	$115^{\circ} 58'$	$116^{\circ} 0'$	2	—
$r'o' = (201) : (111) \dots$	—	—	—	$34^{\circ} 35'$	—	—
$o'p = (111) : (110) \dots$	—	—	—	$92^{\circ} 49'$	—	—
$pr' = (110) : (201) \dots$	18	$53^{\circ} 23' - 53^{\circ} 38'$	$53^{\circ} 28'$	$53^{\circ} 37'$	9	51 58
$r'p = (201) : (110) \dots$	16	$127^{\circ} 24' - 127^{\circ} 38'$	$127^{\circ} 30'$	$127^{\circ} 23'$	7	—
Total number of measurements from 10 crystals		407				



*Habit.*—That characteristic of the potassium salts of the series, namely, short prismatic parallel to the vertical axis  $c$ , to tabular parallel to  $c\{001\}$ , with  $c\{001\}$  and  $p\{110\}$  vastly predominating,  $q\{011\}$  being very small. A typical crystal is represented in fig. 1.

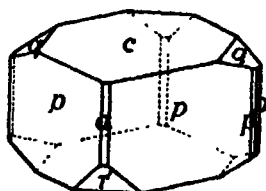


FIG. 1.

The very small faces of  $r'\{\bar{2}01\}$  were usually the only other faces visible, but on two measured crystals narrow strip-faces of  $a\{100\}$  and  $b\{010\}$  were present. One good little face of the prism  $p'\{120\}$  was present on one of the measured crystals. The  $p$ -faces of this salt were generally more affected by striation than those of the other salts of the group, and more difficulty was experienced, but eventually overcome, in finding ten crystals adequately free from this fault. The crystal measured by Topsøe was obviously much affected by striation, his value for the angle  $pp = (110) : (\bar{1}\bar{1}0)$  being much too small.

*Cleavage.*—Excellent parallel to  $r'\{\bar{2}01\}$ .

*Relative Density.*—Six determinations were made by the immersion method using methylene iodide and benzene mixture.

I.	Density for $18^\circ 4/4^\circ$ .....	2.5292	For $20^\circ/4^\circ$ .....	2.5288
II.	" $18^\circ 2/4^\circ$ .....	2.5310	" .....	2.5305
III.	" $18^\circ 3/4^\circ$ .....	2.5308	" .....	2.5304
IV.	" $18^\circ 0/4^\circ$ .....	2.5300	" .....	2.5295
V.	" $18^\circ 3/4^\circ$ .....	2.5291	" .....	2.5287
VI.	" $18^\circ 9/4^\circ$ .....	2.5292	" .....	2.5289
				Mean .....
				2.5295

Accepted value for  $20^\circ/4^\circ$ .....2.530.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{527.77}{2.530} = 208.60.$$

Topsøe found the specific gravity 2.514, a value much too low, and the molecular volume correspondingly much too high, 211.5.

*Molecular Distance Ratios* (topic axial ratios).—

$$\chi : \psi : \omega = 6.2197 : 8.2688 : 4.1856.$$

*Orientation of Optical Ellipsoid.*—Plane of optic axes  $b\{010\}$ . Sign of double refraction, positive. The first median line is the  $y$  axis of the indicatrix, and the second median line is  $a$ .

Extinction Direction (2M.L.) in Symmetry Plane.

Plate I..... $5^{\circ} 21'$ ,      Plate II..... $5^{\circ} 25'$ ,      Mean..... $5^{\circ} 23'$ ,

behind the normal to  $c(001)$ . As the latter is  $14^{\circ} 17'$  in front of the vertical axis  $c$ , the second median line lies  $8^{\circ} 54'$  in front of the vertical axis  $c$ . The first median line lies  $5^{\circ} 23'$  above the inclined axis  $a$ . *Topsøe* and *Christiansen* found  $3^{\circ} 25'$  for the latter. Fig. 2 will render these facts clear.

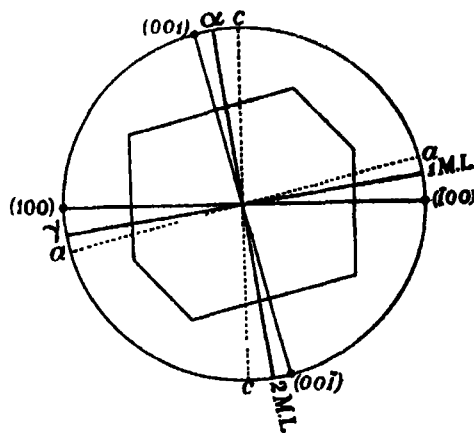


FIG. 2.

*Optic Axial Angle.*—Results with three pairs of plates ground perpendicular to the first and second median lines. Plate 3 was so thick and therefore absorptive, that 2E was not clearly measurable with it.

Apparent Optic Axial Angle in Air, 2E, of KCo Selenate.

Light.	Plate 1.	Plate 2.	Mean 2E.
Li.....	$103^{\circ} 51'$	$103^{\circ} 34'$	$103^{\circ} 43'$
C.....	$103^{\circ} 53'$	$103^{\circ} 40'$	$103^{\circ} 49'$
Na.....	$104^{\circ} 28'$	$104^{\circ} 21'$	$104^{\circ} 25'$
Tl.....	$105^{\circ} 12'$	$105^{\circ} 23'$	$105^{\circ} 18'$
Cd.....	$105^{\circ} 38'$	$105^{\circ} 53'$	$105^{\circ} 46'$

*Topsøe* and *Christiansen* obtained  $106^{\circ} 58'$  for 2E for sodium light.

## Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H <sub>a</sub> .	No. of plate perp. 2 M.L.	Observed 2H <sub>a</sub> .	Calculated 2V <sub>a</sub> .	Mean 2V <sub>a</sub> .
Li.....	{ 1 .....	58 54	1a	103 44	62 7	62 12
	{ 2 .....	58 40	2a	103 31	62 17	
	{ 3 .....	58 37	3a	103 40	62 11	
C .....	{ 1 .....	58 34	1a	103 41	62 8	62 13
	{ 2 .....	58 40	2a	103 38	62 18	
	{ 3 .....	58 37	3a	103 38	62 12	
Na .....	{ 1 .....	58 30	1a	103 17	62 14	62 19
	{ 2 .....	58 36	2a	103 2	62 24	
	{ 3 .....	58 33	3a	103 7	62 30	
Tl .....	{ 1 .....	58 24	1a	102 52	62 18	62 27
	{ 2 .....	58 32	2a	102 24	62 34	
	{ 3 .....	58 28	3a	102 29	62 29	

Owing to the strong absorption by these ruby-red crystals of light of wave-lengths beyond that of the thallium green line, the true optic axial angle could only be determined by observations of 2H<sub>a</sub> and 2H<sub>b</sub> in bromonaphthalene so far as for that colour. In the case of 2E, observations were found possible as far as the wave-length of the green cadmium line.

Topsøe and Christiansen found 63° 52' for 2V<sub>a</sub> for sodium light.

*Dispersion of the Median Lines.*—This was determined by immersion in monochlorobenzene, the refractive index of which, 1.5248 for Na light, is almost absolutely identical with the mean index of the crystals, 1.5252 for Na light. It proved to be exceedingly small, less than 5', and the brushes showed no colour at all on their margins (except the pale red of the section itself).

*Effect of Temperature on Optic Axial Angle.*—2E was determined with section 1 for 80° C., and found to be 110° 6' for Na light. Hence the angle in air increases 5½° on heating from the ordinary temperature to 80° C.

*Refractive Indices.*—Results with six 60°-prisms, each ground to yield two indices. The images were clearly discernible even for Cd, F, and G light.

## Refractive Indices of Potassium Cobalt Selenate.

Light.	α.	β.	γ.
Li .....	1.5122	1.5181	1.5241
C .....	1.5127	1.5186	1.5247
Na .....	1.5158	1.5218	1.5280
Tl .....	1.5190	1.5250	1.5315
Cd .....	1.5211	1.5271	1.5335
F .....	1.5231	1.5291	1.5355
G .....	1.5252	1.5314	1.5332

Mean of α, β, and γ for Na light = 1.5252.

α = Vibration direction parallel to second median line, 8° 54' in front of axis c.

β = " " " symmetry axis b.

γ = " " " first median line, 5° 38' above axis α.

Double refraction, Na<sub>γ-α</sub> = 0.0222.

General formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.5026 + \frac{813}{\lambda^2} - \frac{127}{\lambda^3} - \frac{4}{\lambda^4} + \frac{606}{\lambda^5} + \frac{800}{\lambda^6} + \frac{000}{\lambda^7} + \frac{000}{\lambda^8} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.5026 be diminished by 0.0060, and the  $\gamma$  indices if it be increased by 0.0163.

*Observations at 70°* indicated that the refractive indices diminish by about 0.0026 for a rise of 60° of temperature.

The values of *Topse* and *Christiansen* were: for  $\beta$ , line C 1.5162, line D 1.5195, line F 1.5270; the  $\alpha$  and  $\gamma$  values were only obtained indirectly and for line D only; they are given as 1.5135 and 1.5358.

*Axial Ratios of the Optical Ellipsoid*—

$$\alpha : \beta : \gamma = 0.9960 : 1 : 1.0106, \quad a : b : c = 1.0040 : 1 : 0.9895.$$

#### Molecular Optical Constants.

	Axis of optical indicatrix.	$\alpha$ .	$\beta$ .	$\gamma$ .
Lorenz .....	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ .....	{ C 0.1187	0.1199	0.1230
		{ G 0.1220	0.1231	0.1263
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ .....	{ C 62.66	63.27	64.91
		{ G 64.86	64.98	66.68
	Specific dispersion, $n_d - n_c$ .....	0.0033	0.0032	0.0033
Gladstone ...	Molecular dispersion, $m_d - m_c$ .....	1.70	1.71	1.77
	Molecular refraction, $\frac{n^2-1}{d} M$ .....	C 106.95	108.18	111.54

Mean molecular refraction (Gladstone),  $\frac{1}{3} (\alpha + \beta + \gamma) = 108.89$ .

*Rubidium Cobalt Selenate*,  $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

*Crystal System*.—Monoclinic. Class No. 5, holohedral-prismatic.

*Axial Angle*.— $\beta = 105^\circ 14'$ .

*Ratio of Axes*.— $a : b : c = 0.7427 : 1 : 0.5019$ .

*Forms observed*.— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $q\{011\}$ ,  $r'\{\bar{2}01\}$ ,  $\sigma'\{\bar{1}11\}$ .

*Habit*.—More or less tabular parallel to  $c\{001\}$ , to short prismatic parallel to the vertical axis  $c$  as prism axis. The greater portion of the numerous crops obtained were of the former type; a typical specimen is shown in fig. 3

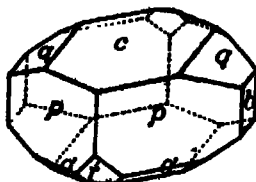


FIG. 3.

## Interfacial Angles of Rubidium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated	Diff.
$\{ao = (100) : (001) \dots$	—	° ' — ° '	° ' —	74 48	'
$as = (100) : (101) \dots$	—	—	—	45 48	
$ac = (101) : (001) \dots$	—	—	—	28 58	
$\{oa' = (001) : (201) \dots$	15	63 41-63 58	63 48	63 43	5
$oa'' = (001) : (101) \dots$	—	—	—	38 25	
$a'r' = (101) : (201) \dots$	—	—	—	25 18	
$\{ra = (201) : (100) \dots$	—	—	—	41 81	
$ro = (201) : (001) \dots$	15	116 2-116 19	116 12	116 17	5
$ap = (100) : (110) \dots$	—	—	—	35 38	
$pp' = (110) : (120) \dots$	—	—	—	19 28	
$p'b = (120) : (010) \dots$	—	—	—	34 54	
$pp'' = (110) : (180) \dots$	—	—	—	29 26	
$p''b = (180) : (010) \dots$	—	—	—	24 56	
$p'b = (110) : (010) \dots$	37	54 15-54 31	54 22	*	
$pp = (110) : (110) \dots$	21	71 8-71 29	71 16	71 16	0
$pp = (110) : (110) \dots$	22	108 24-108 52	108 43	108 44	1
$\{oa = (001) : (011) \dots$	39	25 34-25 58	25 50	*	
$qb = (011) : (010) \dots$	36	64 3-64 30	64 10	64 10	0
$qq = (011) : (011) \dots$	20	128 6-128 37	128 20	128 20	0
$\{ao = (100) : (111) \dots$	—	—	—	49 0	
$oq = (111) : (011) \dots$	—	—	—	27 19	
$aq = (100) : (011) \dots$	—	—	—	76 19	
$qo' = (011) : (111) \dots$	—	—	—	34 37	
$o'a = (111) : (100) \dots$	—	—	—	69 4	
$oo = (001) : (111) \dots$	—	—	—	34 35	
$op = (111) : (110) \dots$	—	—	—	43 5	
$\{op = (001) : (110) \dots$	40	77 33-77 47	77 40	*	
$po' = (110) : (111) \dots$	11	57 23-57 46	57 37	57 42	5
$o'o = (111) : (001) \dots$	11	44 34-44 52	44 41	44 38	3
$po = (110) : (001) \dots$	40	102 10-102 27	102 19	102 20	1
$\{oa = (010) : (121) \dots$	—	—	—	54 16	
$no = (121) : (111) \dots$	—	—	—	15 57	
$bo = (010) : (111) \dots$	—	—	—	70 13	
$os = (111) : (101) \dots$	—	—	—	19 47	
$\{bo' = (010) : (111) \dots$	9	65 8-65 18	65 13	65 14	1
$o's' = (111) : (101) \dots$	—	—	—	24 46	
$o'o' = (111) : (111) \dots$	4	49 23-49 41	49 34	49 32	2
$\{oq = (101) : (011) \dots$	—	—	—	28 3	
$qp = (011) : (110) \dots$	35	86 14-86 46	86 29	86 28	1
$ps = (110) : (101) \dots$	—	—	—	55 29	
$pq = (110) : (011) \dots$	35	93 16-93 46	93 31	93 32	1
$\{s'q = (101) : (011) \dots$	—	—	—	45 9	
$qn = (011) : (121) \dots$	—	—	—	26 39	
$np = (121) : (110) \dots$	—	—	—	36 51	
$qp = (011) : (110) \dots$	36	63 21-63 46	63 33	63 30	3
$p's' = (110) : (101) \dots$	—	—	—	71 21	
$pq = (110) : (011) \dots$	36	116 15-116 42	116 28	116 30	2
$\{r'o' = (201) : (111) \dots$	12	34 39-35 0	34 51	34 49	2
$pr' = (111) : (110) \dots$	12	92 35-92 58	92 45	92 40	5
$pr' = (110) : (201) \dots$	32	52 15-52 32	52 24	52 31	7
$rp = (201) : (110) \dots$	32	127 29-127 44	127 36	127 29	7
Total number of measurements from 10 crystals	550				

The  $q$ -faces were relatively larger, compared with the  $c$ -faces, than in the case of the potassium salt, but the  $c$ -faces in most cases still predominated as the principal faces of the tablet.

The  $p$ -faces were always important, and their lesser or greater depth determined the tabular or prismatic character of the crystals.

The faces of  $r'$  were almost invariably small, and those of  $o'$  were but narrow strips modifying the  $cp$  edges. The clinopinakoid faces  $b$  were also small, but usually gave excellent reflections of the signal. Ten excellent crystals were measured.

*Cleavage*.—Parallel to  $r'\{\bar{2}01\}$ , perfect.

*Relative Density*.—Six determinations were made by the immersion method.

I. Density for $16^{\circ}8/4^{\circ}$ .....	2.8367	For $20^{\circ}/4^{\circ}$ .....	2.8358
II. " " $17^{\circ}9/4^{\circ}$ .....	2.8368	" " " .....	2.8362
III. " " $18^{\circ}2/4^{\circ}$ .....	2.8390	" " " .....	2.8385
IV. " " $17^{\circ}3/4^{\circ}$ .....	2.8379	" " " .....	2.8371
V. " " $18^{\circ}8/4^{\circ}$ .....	2.8375	" " " .....	2.8372
VI. " " $18^{\circ}4/4^{\circ}$ .....	2.8385	" " " .....	2.8380
		Mean .....	2.8371

Accepted value for  $20^{\circ}/4^{\circ}$ .....**2.837**.

*Molecular Volume*.— $\frac{M}{d} = \frac{619.87}{2.837} = 218.49$ .

*Molecular Distance* (topic axial) ratios.—

$$\chi : \psi : \omega = 6.2901 : 8.4693 : 4.2508.$$

*Orientation of Optical Ellipsoid*.—Plane of optic axes,  $b\{010\}$ . Sign of double refraction, positive. The first median line is the  $\gamma$  axis of the indicatrix, and the second median line is  $\alpha$ .

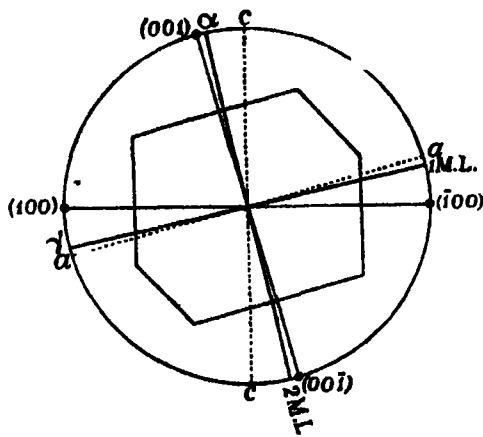


FIG. 4.

## Extinction Direction (2M.L.) in Symmetry Plane.

Plate I... $1^{\circ} 24'$ , Plate II... $3^{\circ} 2'$ . Plate III... $2^{\circ} 45'$ , Mean... $2^{\circ} 24'$ , behind the normal to  $c(001)$ . As that normal is  $15^{\circ} 14'$  in front of the vertical axis  $c$ , the second median line lies  $12^{\circ} 50'$  in front of the vertical axis  $c$ . The first median line lies  $2^{\circ} 24'$  above the inclined axis  $a$ . Fig. 4 will render this clear.

*Optic Axial Angle.*—Results with three pairs of section-plates perpendicular to the two median lines. Plate 2 did not quite admit of 2E being fully visible, being narrow and the angle in air very wide.

## Apparent Optic Axial Angle in Air, 2E, of RbCo Selenate.

Light.	Plate 1.	Plate 3.	Mean 2E.
Li.....	$131^{\circ} 40'$	$130^{\circ} 35'$	$131^{\circ} 8'$
C ..	$131^{\circ} 48'$	$130^{\circ} 40'$	$131^{\circ} 14'$
Na ..	$132^{\circ} 40'$	$131^{\circ} 30'$	$132^{\circ} 5'$
Tl ..	$133^{\circ} 30'$	$132^{\circ} 30'$	$133^{\circ} 0'$

## Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H <sub>a</sub> .	No. of plate perp. 2 M.L.	Observed 2H <sub>a</sub> .	Calculated 2V <sub>a</sub> .	Mean 2V <sub>a</sub> .
Li .....	{ 1 .....	$68^{\circ} 56'$	1a	$94^{\circ} 40'$	$73^{\circ} 44'$	$73^{\circ} 42'$
	{ 2 .....	$67^{\circ} 9'$	2a	$94^{\circ} 38'$	$73^{\circ} 54'$	
	{ 3 .....	$66^{\circ} 26'$	3a	$94^{\circ} 38'$	$73^{\circ} 28'$	
O .....	{ 1 .....	$66^{\circ} 58'$	1a	$94^{\circ} 35'$	$73^{\circ} 44'$	$73^{\circ} 41'$
	{ 2 .....	$67^{\circ} 5'$	2a	$94^{\circ} 35'$	$73^{\circ} 53'$	
	{ 3 .....	$66^{\circ} 22'$	3a	$94^{\circ} 24'$	$73^{\circ} 26'$	
Na .....	{ 1 .....	$66^{\circ} 34'$	1a	$94^{\circ} 11'$	$73^{\circ} 41'$	$73^{\circ} 37'$
	{ 2 .....	$66^{\circ} 46'$	2a	$94^{\circ} 15'$	$73^{\circ} 47'$	
	{ 3 .....	$66^{\circ} 3'$	3a	$94^{\circ} 2'$	$73^{\circ} 23'$	
Tl ..	{ 1 .....	$66^{\circ} 15'$	1a	$93^{\circ} 47'$	$73^{\circ} 38'$	$73^{\circ} 33'$
	{ 2 .....	$66^{\circ} 27'$	2a	$93^{\circ} 53'$	$73^{\circ} 40'$	
	{ 3 .....	$65^{\circ} 46'$	3a	$93^{\circ} 36'$	$73^{\circ} 20'$	

The absorption by these ruby red crystals did not admit of accurate measurements beyond the green.

*Dispersion of the Median Lines.*—This was determined by immersion of the sections perpendicular to the first median line in monochlorobenzene, the refractive index of which is almost identical with the mean index of the crystals. The dispersion proved to be exceedingly small, less than  $5'$ , so small, indeed, that its direction was not determinable with certainty. The vertices of the brushes were quite black, as seen in this liquid, with no perceptible colour at the margins except the natural red of the section-plates themselves.

*Effect of Temperature on Optic Axial Angle.*—Determinations of 2E at 75° C. indicated that the angle in air increases 5° on raising the temperature 65° from the ordinary temperature to 75° C.

*Refractive Indices.*—Results obtained with six 60°-prisms, each ground to afford two indices directly.

**Refractive Indices of Rubidium Cobalt Selenate.**

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li .. .. .	1·5163	1·5220	1·5229
O .. .. .	1·5168	1·5225	1·5234
Na .. .. .	1·5199	1·5256	1·5269
Tl .. .. .	1·5232	1·5290	1·5404
Cd .. .. .	1·5252	1·5311	1·5425
F .. .. .	1·5273	1·5332	1·5446
G .. .. .	1·5333	1·5393	1·5508

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1·5275.

$\alpha$  = Vibration direction parallel to second median line, 12° 50' in front of axis c.

$\beta$  = " " " symmetry axis b.

$\gamma$  = " " " first median line, 2° 24' above axis a.

Double refraction,  $N_{\alpha\gamma-\alpha}$  = 0·0170.

General formula  $\beta$ , corrected to a vacuum :—

$$\beta = 1\cdot5098 + \frac{571\ 580}{\lambda^2} - \frac{316\ 900\ 000\ 000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced by the formula if the constant 1·5098 be diminished by 0·0057, and the  $\gamma$  indices if it be increased by 0·0113.

*Observations at 70°* indicated that the refractive indices diminish with rise of temperature, to the extent of 0·0025 for 60° rise of temperature.

*Axial Ratios of the Optical Ellipsoid*—

$$\alpha : \beta : \gamma = 0\cdot9963 : 1 : 1\cdot0074, \quad a : b : c = 1\cdot0037 : 1 : 0\cdot9926.$$

**Molecular Optical Constants.**

	Axis of optical indicatrix.	$\alpha$ .	$\beta$ .	$\gamma$ .
Lorenz .....	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n \dots \dots \dots$	{ O 0·1066	0·1076	0·1095
		{ G 0·1094	0·1105	0·1124
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m \dots \dots \dots$	{ O 66·08	66·69	67·86
		{ G 67·84	68·45	69·69
	Specific dispersion, $n_D - n_C \dots \dots \dots$	0·0028	0·0029	0·0029
Gladstone ...	Molecular dispersion, $m_D - m_C \dots \dots \dots$	1·76	1·79	1·83
	Molecular refraction, $\frac{n^2-1}{d} M \dots \dots \dots$	C 112·92	114·16	116·54

Mean molecular refraction (Gladstone),  $\frac{1}{3}(\alpha + \beta + \gamma) = 114\cdot54$ .



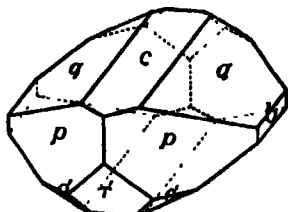
*Cæsium Cobalt Selenate*,  $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Crystal System*.—Monoclinic. Class No. 5, holohedral-prismatic.*Axial Angle*.— $\beta = 106^\circ 18'$ .*Ratio of Axes*.— $a : b : c = 0.7310 : 1 : 0.4989$ .*Forms observed*.— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $q\{011\}$ ,  $r'\{\bar{2}01\}$ ,  $o'\{\bar{1}11\}$ .*Habit*.—Prismatic parallel to inclined axis  $a$ . A typical crystal is shown in fig. 5.

FIG. 5.

The characteristics of the cæsium salts of this grand series are well shown by cæsium cobalt selenate, namely, narrow  $c\{001\}$  faces and broader  $q\{011\}$  faces. The great majority of the crystals showed no faces of either  $b\{010\}$  or  $o'\{\bar{1}11\}$ , and not infrequently also no  $r'\{\bar{2}01\}$  faces, the only forms developed being  $c\{001\}$ ,  $q\{011\}$ , and  $p\{110\}$ . Occasionally an excellent face of  $b\{010\}$  was found on the larger crystals.

*Cleavage*.—Perfect parallel  $r'\{\bar{2}01\}$ .*Relative Density*.—Six determinations were carried out by the immersion method.

I. Density for $19^\circ 2/4^\circ$ ...	3.0938	For $20^\circ/4^\circ$ .....	3.0986
II. " 17° 9/4° .....	3.0939	" .....	3.0983
III. " 17° 9/4° .....	3.0924	" .....	3.0918
IV. " 18° 9/4° ... ..	3.0958	" .....	3.0955
V. " 16° 7/4° .....	3.0954	" .....	3.0944
VI. " 17° 2/4° ... ..	3.0947	" .....	3.0988
		Mean .....	3.0937

Accepted value for  $20^\circ/4^\circ$ .....3.094.*Molecular Volume*.— $\frac{M}{d} = \frac{713.87}{3.094} = 230.73$ .*Molecular Distance* (topic axial) ratios.—

$$\chi : \psi : \omega = 6.3618 : 8.7028 : 4.3418.$$

*Orientation of Optical Ellipsoid*.—Plane of optic axes  $b\{010\}$ . Sign of double refraction positive. The first median line is the  $\gamma$  axis of the indicatrix, and the second line median is  $\alpha$ .

## Interfacial Angles of Cæsium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ao = (100) : (001)$	—	—	—	73 43	—
$as = (100) : (101)$	—	—	—	44 55	—
$so = (101) : (001)$	—	—	—	28 47	—
$or' = (001) : (201)$	15	64 31-64 59	64 48	64 46	2
$os' = (001) : (101)$	—	—	—	39 0	—
$s'r' = (101) : (201)$	—	—	—	25 46	—
$r'a = (201) : (100)$	—	—	—	41 32	—
$r'o = (201) : (001)$	15	115 3-115 33	115 13	115 14	1
$ap = (100) : (110)$	—	—	—	35 3.5	—
$pp' = (110) : (120)$	—	—	—	19 28	—
$p'b = (120) : (010)$	—	—	—	35 28	—
$pp''' = (110) : (130)$	—	—	—	29 31	—
$p'''b = (130) : (010)$	—	—	—	25 25	—
$pb = (110) : (010)$	4	54 56-54 59	54 58	54 56.5	1.5
$pp = (110) : (110)$	22	69 53-70 20	70 7	—	—
$pp = (110) : (110)$	22	109 43-110 18	109 53	109 53	0
$oq = (001) : (011)$	43	25 26-25 43	25 35	—	—
$qb = (011) : (010)$	8	64 23-64 26	64 24	64 25	1
$qq = (011) : (011)$	21	128 41-128 54	128 49	128 50	1
$ao = (100) : (111)$	—	—	—	48 6	—
$oq = (111) : (011)$	—	—	—	27 14	—
$aq = (100) : (011)$	—	—	—	75 20	—
$qo' = (011) : (111)$	—	—	—	35 13	—
$o'a = (111) : (100)$	—	—	—	69 28	—
$oo = (001) : (111)$	—	—	—	34 14	—
$op = (111) : (110)$	—	—	—	42 29	—
$op = (001) : (110)$	42	76 32-76 52	76 43	—	—
$po' = (110) : (111)$	7	58 0-58 18	58 8	58 10	2
$o'o = (111) : (001)$	11	44 58-45 18	45 11	45 7	4
$pe = (110) : (001)$	42	103 8-103 27	103 16	103 17	1
$bn = (010) : (121)$	—	—	—	54 51	—
$no = (121) : (111)$	—	—	—	15 45	—
$bo = (010) : (111)$	—	—	—	70 36	—
$os = (111) : (101)$	—	—	—	19 24	—
$bo' = (010) : (111)$	6	65 17-65 24	65 21	65 17	4
$o's' = (111) : (101)$	—	—	—	24 43	—
$o'o' = (111) : (111)$	6	49 13-49 26	49 22	49 26	4
$sq = (101) : (011)$	—	—	—	37 46	—
$qp = (011) : (110)$	43	87 34-87 52	87 42	87 40	2
$ps = (110) : (101)$	—	—	—	54 34	—
$pq = (110) : (011)$	43	92 6-92 26	92 18	92 20	2
$s'q = (101) : (011)$	—	—	—	45 30	—
$qn = (011) : (121)$	—	—	—	26 30	—
$np = (121) : (110)$	—	—	—	36 25	—
$qp = (011) : (110)$	42	62 42-63 17	62 55	62 55	0
$ps' = (110) : (101)$	—	—	—	71 35	—
$pq = (110) : (011)$	41	116 48-117 17	117 5	117 5	0
$r'o' = (201) : (111)$	10	34 55-35 18	35 8	35 7	1
$o'p = (111) : (110)$	9	92 35-92 44	92 39	92 40	1
$pr' = (110) : (201)$	21	52 1-52 20	52 14	52 13	1
$r'p = (201) : (110)$	21	127 38-127 57	127 46	127 47	1
Total number of measurements from 11 crystals	494				

## Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I..... $2^{\circ} 40'$ ,    Plate II..... $3^{\circ} 13'$ ,    Plate III..... $3^{\circ} 21'$ ,Mean extinction angle..... $3^{\circ} 5'$ ,

in front of the normal to  $c(001)$ . As that normal is already  $16^{\circ} 18'$  in front of the vertical axis  $c$ , the second median line lies  $19^{\circ} 23'$  in front of the vertical axis  $c$ . The first median line lies  $3^{\circ} 5'$  below the inclined axis  $a$ . Fig. 6 will render the position plain.

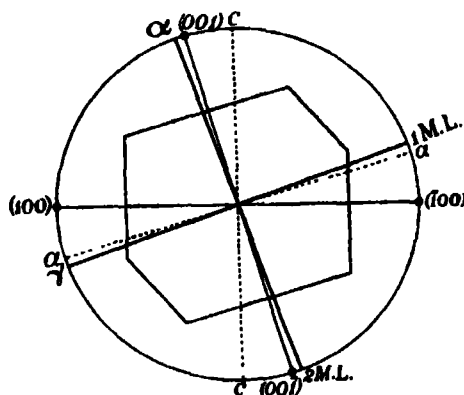


FIG. 6.

*Optic Axial Angle.*—Results for three pairs of section-plates, ground perpendicular to the two median lines. The optic axial angle is so large that it does not emerge in air.

*Cæsium Cobalt Selenate.*

## Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_a$ .	Calculated $2V_a$ .	Mean $2V_a$ .
Li.....	{ 1 .....	79 16	1a	84 16	87 7	87 11
	{ 2 .....	79 20	2a	84 21	87 6	
	{ 3 .....	79 34	3a	84 13	87 20	
C .....	{ 1 .....	79 10	1a	84 16	87 4	87 8
	{ 2 .....	79 14	2a	84 20	87 3	
	{ 3 .....	79 28	3a	84 12	87 16	
Na .....	{ 1 .....	78 34	1a	84 12	86 44	86 46
	{ 2 .....	78 44	2a	84 17	86 47	
	{ 3 .....	78 46	3a	84 5	86 54	
Ti.....	{ 1 .....	78 0	1a	84 9	86 24	86 32
	{ 2 .....	78 14	2a	84 9	86 33	
	{ 3 .....	78 13	3a	83 55	86 40	

Measurements of  $2H_a$  and  $2H_c$  were only possible as far as the green of the spectrum, on account of the large absorption by these red crystals, thick plates being required in order to yield clear interference figures.

*Dispersion of the Median Lines.*—This was determined by immersion of the section-plates perpendicular to the first median line in oil of cloves, the refractive index of which for sodium light, 1·5409 (re-determined at the time), is practically identical with that (mean of all three indices, 1·5402) of the crystals. It was found that the median lines are dispersed 10' in the symmetry plane, so that for green thallium light the first median line is nearer to the inclined axis *a* by 10' than for red C-light.

*Refractive Indices.*—Results with six 60°-prisms, each ground to afford two indices directly.

Refractive Indices of Cæsium Cobalt Selenate.

Light.	<i>a.</i>	<i>β.</i>	<i>γ.</i>
Li .....	1·5316	1·5380	1·5412
C .....	1·5321	1·5385	1·5418
Na .....	1·5354	1·5399	1·5453
Tl .....	1·5389	1·5434	1·5489
Cd .....	1·5409	1·5454	1·5510
F .....	1·5430	1·5475	1·5531
G .....	1·5492	1·5539	1·5596

Mean of *a*, *β*, and *γ* for Na light = 1·5402.

*a* = Vibration direction parallel to second median line, 19° 23' in front of axis *c*.

*β* = " " " symmetry axis *b*.

*γ* = " " " first median line, 8° 5' below axis *a*.

Double refraction, Na<sub>*γ-a*</sub> = 0·0099.

General formula for the intermediate refractive index *β*, corrected to a vacuum (correction + 0·0004) :—

$$\beta = 1\cdot5205 + \frac{784\ 570}{\lambda^2} - \frac{3\ 376\ 600\ 000\ 000}{\lambda^4} + \dots$$

The *a* indices are also reproduced very closely by the formula if the constant 1·5205 be diminished by 0·0045 and the *γ* indices if the constant be increased by 0·0054.

*Observations at 70° C.* showed that the refractive indices are diminished by about 0·0018 (varying from 0·0016 to 0·0020) for 60° rise of temperature.

*Axial Ratios of the Optical Ellipsoid*—

$$a : \beta : \gamma = 0\cdot9971 : 1 : 1\cdot0035, \quad a : b : c = 1\cdot0029 : 1 : 0\cdot9965.$$

## Molecular Optical Constants.

	Axis of optical indicatrix.		$\alpha$ .	$\beta$ .	$\gamma$ .
Lorenz .....	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ .....	{ C	0·1002	0·1009	0·1017
		{ G	0·1028	0·1036	0·1044
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ ..	{ C	71·51	72·00	72·59
		{ G	73·41	73·93	74·56
	Specific dispersion, $n_d - n_c$ .....		0·0026	0·0027	0·0027
Gladstone ..	Molecular dispersion, $m_d - m_c$ ..		1·90	1·93	1·97
	Molecular refraction, $\frac{n^2-1}{d} M$ ... ..	. C	122·77	123·79	125·01

Mean molecular refraction (Gladstone),  $\frac{1}{3}(\alpha + \beta + \gamma) = 123·86$ .

*Ammonium Cobalt Selenate*  $(\text{NH}_4)_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

*Crystal System*.—Monoclinic. Class No. 5, holohedral-prismatic.

*Axial Angle*.— $\beta = 106^\circ 23'$ . The same value was found by Topsøe.

*Ratio of Axes*.— $a : b : c = 0·7449 : 1 : 0·5031$ .

Topsøe's values  $0·7414 : 1 : 0·5037$ .

*Forms observed*.— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $p'\{120\}$ ,  $q\{011\}$ ,  $m\{021\}$ ,  $o'\{\bar{1}11\}$ ,  $r'\{\bar{2}01\}$ .

The forms  $p'\{120\}$  and  $m\{021\}$  were not observed by Topsøe.

*Habit*.—More or less tabular parallel to  $c\{001\}$ , but with the  $q\{011\}$  faces also considerably developed. A typical crystal is represented in Fig. 7.

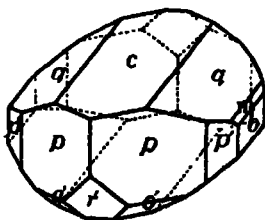


FIG. 7.

The type is thus intermediate between that of the potassium salt shown in fig. 1 and that of the caesium salt represented in fig. 5. It is not unlike that of the rubidium salt (fig. 3), but the faces of  $q\{011\}$  and  $r'\{\bar{2}01\}$  were generally larger. The relative importance of the subsidiary faces was generally more or less as shown in fig. 7. Some excellent little faces of  $p'\{120\}$  were observed, affording sharp signal images. One good little face of the very rare clinodomal form  $m\{021\}$  was discovered on one of the twelve crystals measured, which belonged to three different crops of particularly good crystals. Some relatively large and excellently reflecting faces of the clinopinakoid  $b\{010\}$  were present on the crystals of certain crops.

## Interfacial Angles of Ammonium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Topsee's values.
$ac = (100) : (001)$	—	—	—	73 37	—	—
$as = (100) : (101)$	—	—	—	45 3	—	—
$sc = (101) : (001)$	—	—	—	28 34	—	—
$cr' = (001) : (201)$	21	64 15-64 51	64 35	64 30	5	64 58
$cs' = (001) : (101)$	—	—	—	38 42	—	—
$s'r' = (101) : (201)$	—	—	—	25 48	—	—
$r'a = (201) : (100)$	—	—	—	41 53	—	—
$r'c = (201) : (001)$	21	115 12-115 45	115 25	115 30	5	—
$ap = (100) : (110)$	—	—	—	35 32	—	—
$pp' = (110) : (120)$	12	19 22-19 31	19 27	19 28	1	—
$p'b = (120) : (010)$	11	34 55-35 7	35 2	35 0	2	—
$pp''' = (110) : (130)$	—	—	—	29 27	—	—
$p'''b = (130) : (010)$	—	—	—	25 1	—	—
$pb = (110) : (010)$	48	54 16-54 49	54 28	*	—	54 35
$pp = (110) : (110)$	25	70 50-71 18	71 3	71 4	1	70 51
$cp = (001) : (011)$	41	25 41-25 57	25 46	*	—	25 41
$qm = (011) : (021)$	1	—	18 16	18 14	2	—
$mb = (021) : (010)$	1	—	45 56	46 0	4	—
$qb = (011) : (010)$	43	64 4-64 22	64 14	64 14	0	64 17
$ao = (100) : (111)$	—	—	—	48 17	—	—
$oq = (111) : (011)$	—	—	—	27 0	—	—
$aq = (100) : (011)$	—	—	—	75 17	—	—
$qo' = (011) : (111)$	—	—	—	34 50	—	—
$o'a = (111) : (100)$	—	—	—	69 53	—	—
$co = (001) : (111)$	—	—	—	34 10	—	—
$op = (111) : (110)$	—	—	—	42 34	—	—
$cp = (001) : (110)$	40	76 35-76 52	76 44	*	—	76 43
$po' = (110) : (111)$	14	58 2-59 38	58 18	58 19	1	—
$o'e = (111) : (001)$	14	44 41-45 17	44 56	44 57	1	—
$pr = (110) : (001)$	40	103 10-103 23	103 16	103 16	0	103 17
$bn = (010) : (121)$	—	—	—	54 33	—	—
$no = (121) : (111)$	—	—	—	15 51	—	—
$bo = (010) : (111)$	—	—	—	70 24	—	—
$os = (111) : (101)$	—	—	—	19 36	—	—
$bo' = (010) : (111)$	7	65 5-65 10	65 7	65 3	4	—
$o's' = (111) : (101)$	—	—	—	24 57	—	—
$o'o' = (111) : (111)$	4	49 45-49 50	49 48	49 54	6	—
$sq = (101) : (011)$	—	—	—	37 44	—	—
$qp = (011) : (110)$	40	87 17-87 34	87 24	87 22	2	87 26
$ps = (110) : (101)$	—	—	—	54 54	—	—
$pq = (110) : (011)$	40	92 27-92 47	92 36	92 38	2	—
$s'q = (101) : (011)$	—	—	—	45 21	—	—
$qn = (011) : (121)$	—	—	—	26 18	—	—
$np = (121) : (110)$	—	—	—	36 21	—	—
$qp = (011) : (110)$	40	62 32-62 53	62 42	62 39	3	62 40
$ps' = (110) : (101)$	—	—	—	72 0	—	—
$pq = (110) : (011)$	40	117 7-117 28	117 18	117 21	3	—
$r'o' = (201) : (111)$	13	35 1-35 40	35 17	35 17	0	—
$o'm = (111) : (021)$	1	—	36 49	36 41	8	—
$mp = (021) : (110)$	1	—	55 20	55 20	0	—
$o'p = (111) : (110)$	13	91 46-92 21	92 5	92 1	4	—
$pr' = (110) : (201)$	38	52 25-52 45	52 36	52 42	6	52 37
$rp = (201) : (110)$	38	127 6-127 43	127 24	127 18	6	—
Total number of measurements from 12 crystals.....	606					

*Cleavage*.—Perfect parallel  $r'\{201\}$ . There is also a much less well defined cleavage parallel to  $b\{010\}$ .

*Relative Density*.—Six determinations were made by the immersion method.

I. Density for $19^{\circ}2/4^{\circ}$	2.2275	For $20^{\circ}/4^{\circ}$	2.2273
II. " $18^{\circ}3/4^{\circ}$	2.2291	" "	2.2287
III. " $20^{\circ}0/4^{\circ}$	2.2279	" "	2.2279
IV. " $18^{\circ}4/4^{\circ}$	2.2287	" "	2.2283
V. " $18^{\circ}6/4^{\circ}$	2.2273	" "	2.2270
VI. " $18^{\circ}6/4^{\circ}$	2.2302	" "	2.2290
		Mean	2.2282

Accepted value for  $20^{\circ}/4^{\circ}$ .....**2.228**.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{485.93}{2.228} = 218.10.$$

Topsøe obtained the lower value 2.212 for the specific gravity, and consequently also a molecular volume too high, namely, 221.3.

*Molecular Distance* (topic axial) ratios.—

$$\chi : \psi : \omega = 6.3057 : 8.4651 : 4.2587.$$

*Orientation of Optical Ellipsoid*.—Plane of optic axes  $b\{010\}$ . Sign of double refraction, positive. The first median line is the  $\gamma$  axis of the indicatrix, and  $a$  is the second median line.

Extinction Direction (2M.L.) in Symmetry Plane.

Plate I..... $13^{\circ}25'$ ,    Plate II..... $14^{\circ}35'$ ,    Mean..... $14^{\circ}0'$ ,

behind the normal to  $c\{001\}$ . As the latter is  $16^{\circ}23'$  in front of the vertical axis  $c$ , this extinction direction, which is the second median line, lies  $2^{\circ}23'$  in front of the vertical axis  $c$ . The first median line lies  $14^{\circ}0'$  above the inclined axis  $a$ . Topsøe obtained  $2^{\circ}41'$  and  $13^{\circ}42'$  for these two extinction angles. These facts are graphically illustrated in fig. 8.

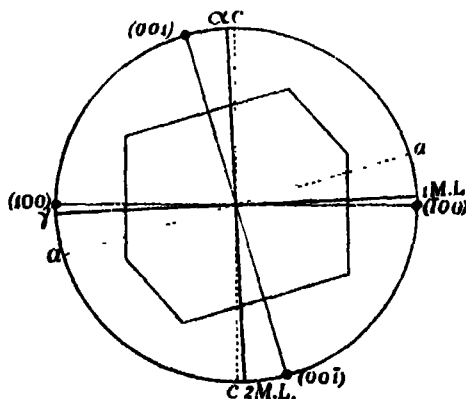


FIG. 8.

*Optic Axial Angle.*—This is so large that  $2E$ , the angle in air, is indeterminate. Results for  $2H_a$ ,  $2H_o$ , and the true angle  $2V_a$ , from three pairs of plates, ground perpendicular to the two bisectrices, are given below. One pair of them were measurable as far as the green of cadmium, the other two pairs only as far as thallium green; beyond these spectrum limits the absorption by these red plates was too great, as thick plates are required to give sharp interference figures.

*Ammonium Cobalt Selenate.*

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
Li	{ 1	74 33	1a	88 14	82 3	82 5
	{ 2	74 30	2a	88 11	82 2	
	{ 3	74 55	3a	88 30	82 9	
C ...	{ 1	74 32	1a	88 10	82 4	82 6
	{ 2	74 29	2a	88 7	82 4	
	{ 3	74 53	3a	88 25	82 10	
Na	{ 1	74 23	1a	87 43	82 12	82 14
	{ 2	74 22	2a	87 38	82 14	
	{ 3	74 39	3a	87 57	82 16	
Tl	{ 1	74 10	1a	87 22	82 16	82 22
	{ 2	74 11	2a	87 8	82 23	
	{ 3	74 24	3a	87 19	82 26	
Cd	{ 1	—	1a	—	—	82 28
	{ 2 ...	74 5	2a	86 50	82 28	
	{ 3 ...	—	3a	—	—	

Topsøe and Christiansen obtained  $82^\circ 1'$  for  $2V_a$ , for sodium light.

*Dispersion of the Median Lines.*—This was determined by immersion in methyl salicylate, the refractive index for sodium light of which, 1.5363, is close to the mean index for that light, 1.5335, for the crystals. The median lines are dispersed  $12'$  in the symmetry plane, so that the first median line is nearer to the inclined axis  $a$  for red C light than for green Tl light, by this amount.

*Refractive Indices.*—The results with the usual six  $60^\circ$ -prisms, each giving two indices, next follow.



## Refractive Indices of Ammonium Cobalt Selenate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Ia . . . . .	1.5228	1.5287	1.5377
C . . . . .	1.5228	1.5292	1.5382
Na . . . . .	1.5261	1.5327	1.5417
Tl . . . . .	1.5294	1.5362	1.5458
Cd . . . . .	1.5315	1.5380	1.5474
F . . . . .	1.5385	1.5401	1.5496
G . . . . .	1.5398	1.5466	1.5562

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5385.

$\alpha$  = Vibration direction parallel to second median line,  $2^\circ 28'$  in front of vertical axis  $c$ .

$\beta$  = " " " symmetry axis  $b$ .

$\gamma$  = " " " first median line,  $14^\circ 0'$  above inclined axis  $a$ .

Double refraction,  $N_{\gamma-\alpha} = 0.0156$ .

General formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.5116 + \frac{893\ 977}{\lambda^2} - \frac{5\ 122\ 300\ 000\ 000}{\lambda^4} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.5116 be diminished by 0.0066, and the  $\gamma$  indices if it be increased by 0.0090.

Observations at  $70^\circ$  indicated that the refractive indices of ammonium cobalt selenate diminish by about 0.0013 for a rise of temperature of  $60^\circ$ .

Topsøe and Christiansen obtained for  $\beta$  the values 1.5280, 1.5311, and 1.5392 for C, D, and F light respectively; and indirectly for  $\alpha$  and  $\gamma$ , for sodium D light only, 1.5244 and 1.5396.

*Axial Ratios of the Optical Ellipsoid.*—

$$\alpha : \beta : \gamma = 0.9957 : 1 : 1.0059, \quad a : b : c = 1.0043 : 1 : 0.9942.$$

## Molecular Optical Constants.

	Axis of optical indicatrix.	$\alpha$ .	$\beta$ .	$\gamma$ .
Lorenz . . . . .	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ . . . . .	C 0.1871	0.1885	0.1404
		G 0.1408	0.1423	0.1443
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ . . . . .	C 66.60	67.28	68.24
		G 68.41	69.12	70.13
Gladstone . . . . .	Specific dispersion, $n_d - n_c$ . . . . .	0.0037	0.0038	0.0039
	Molecular dispersion, $m_d - m_c$ . . . . .	1.81	1.84	1.89
	Molecular refraction, $\frac{n-1}{d} M$ . . . . .	C 114.02	115.42	117.88
		G 114.02	115.42	117.88

Mean molecular refraction (Gladstone),  $\frac{1}{3}(\alpha + \beta + \gamma) = 115.61$ .

*Comparison of Results.*

*Habit.*—The crystals of the potassium, rubidium, and caesium salts of this cobalt group exhibit the habits which have been observed to be characteristic of these respective salts throughout the series, as so far

investigated. They are typified by the relative development of the basal pinakoid  $c\{001\}$  and clinodomal prism  $q\{011\}$ , the former predominating in the potassium salt and the latter in the caesium salt, while in the rubidium salt the two forms are more or less equally developed, the habit of this salt being thus very clearly of intermediate character. The crystals of the ammonium salt are usually very much like those of the intermediate rubidium salt, but the limits are wider, the types shown by the potassium and caesium salts being also each nearly approached in different individuals.

*Crystal Elements and Angles.*—

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Potassium cobalt selenate . . . . .	104° 17'	0·7522 : 1 : 0·5062
Rubidium " " . . . . .	105° 14'	0·7427 : 1 : 0·5019
Ammonium " " . . . . .	106° 23'	0·7449 : 1 : 0·5031
Caesium " " . . . . .	106° 18'	0·7310 : 1 : 0·4989

From the above Table it will be clear that the monoclinic axial angle  $\beta$  for rubidium cobalt selenate is approximately the mean of the corresponding axial angles for the potassium and caesium salts. The axial angle of ammonium cobalt selenate is nearly identical with that of caesium cobalt selenate.

The morphological axial ratios of the rubidium salt are likewise intermediate between the analogous ratios for the potassium and caesium salts. Thus both as regards the axial angle and the axial ratios the constants follow the order of the atomic weights and atomic numbers of the alkali metals present.

Atomic weights:— K = 38·85, Rb = 84·9, Cs = 131·9.

Atomic numbers:—K = 19, Rb = 37, Cs = 55.

The axial ratios of the ammonium salt are intermediate between the two extremes for the group (for the potassium and caesium salts), and fairly close to those for the intermediate rubidium salt. True isomorphism of ammonium cobalt selenate with the three alkali-metallic salts of the cobalt group is thus clearly indicated.

## Comparison of the Interfacial Angles.

Angle.	KCo selenate.	RbCo selenate.	CsCo selenate.	AmCo selenate.
$\left\{ \begin{array}{l} ao = (100) : (001) \\ as = (100) : (101) \\ ac = (101) : (001) \\ ar' = (001) : (201) \\ os' = (001) : (101) \\ s'r' = (101) : (201) \\ sa = (201) : (100) \end{array} \right.$	$\left\{ \begin{array}{l} 75 \frac{0}{43} \\ 46 \frac{27}{29} \\ 29 \frac{16}{68} \\ 62 \frac{58}{38} \\ 38 \frac{6}{24} \\ 52 \frac{52}{41} \\ 19 \frac{19}{41} \end{array} \right.$	$\left\{ \begin{array}{l} 74 \frac{46}{45} \\ 28 \frac{58}{43} \\ 38 \frac{25}{18} \\ 25 \frac{18}{31} \\ 41 \frac{31}{31} \end{array} \right.$	$\left\{ \begin{array}{l} 73 \frac{42}{44} \\ 28 \frac{47}{46} \\ 39 \frac{0}{25} \\ 25 \frac{44}{32} \\ 41 \frac{32}{32} \end{array} \right.$	$\left\{ \begin{array}{l} 73 \frac{37}{45} \\ 28 \frac{34}{30} \\ 38 \frac{42}{43} \\ 25 \frac{43}{43} \\ 41 \frac{53}{53} \end{array} \right.$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pp''' = (110) : (180) \\ p'''b = (180) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} 36 \frac{3}{19} \\ 28 \frac{28}{34} \\ 29 \frac{21}{24} \\ 36 \frac{36}{53} \\ 57 \frac{57}{53} \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{38}{19} \\ 28 \frac{54}{26} \\ 25 \frac{25}{56} \\ 54 \frac{22}{22} \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{4}{28} \\ 35 \frac{28}{81} \\ 25 \frac{25}{25} \\ 54 \frac{56}{56} \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{32}{28} \\ 35 \frac{0}{27} \\ 25 \frac{1}{25} \\ 54 \frac{28}{28} \end{array} \right.$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} 26 \frac{8}{68} \\ 52 \frac{52}{52} \end{array} \right.$	$\left\{ \begin{array}{l} 25 \frac{50}{64} \\ 10 \frac{10}{10} \end{array} \right.$	$\left\{ \begin{array}{l} 25 \frac{35}{64} \\ 25 \frac{25}{25} \end{array} \right.$	$\left\{ \begin{array}{l} 25 \frac{46}{64} \\ 14 \frac{14}{14} \end{array} \right.$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (111) \\ o'a = (111) : (100) \end{array} \right.$	$\left\{ \begin{array}{l} 49 \frac{42}{27} \\ 31 \frac{31}{77} \\ 13 \frac{13}{84} \\ 15 \frac{15}{68} \\ 32 \frac{32}{35} \end{array} \right.$	$\left\{ \begin{array}{l} 49 \frac{0}{27} \\ 19 \frac{19}{76} \\ 19 \frac{19}{34} \\ 37 \frac{37}{69} \\ 4 \frac{4}{4} \end{array} \right.$	$\left\{ \begin{array}{l} 48 \frac{6}{27} \\ 14 \frac{14}{75} \\ 20 \frac{20}{35} \\ 12 \frac{12}{69} \\ 28 \frac{28}{28} \end{array} \right.$	$\left\{ \begin{array}{l} 48 \frac{17}{27} \\ 0 \frac{0}{75} \\ 17 \frac{17}{34} \\ 50 \frac{50}{69} \\ 53 \frac{53}{53} \end{array} \right.$
$\left\{ \begin{array}{l} oo = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (111) \\ o'c = (111) : (001) \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{1}{43} \\ 29 \frac{29}{78} \\ 30 \frac{30}{57} \\ 6 \frac{6}{44} \\ 24 \frac{24}{69} \end{array} \right.$	$\left\{ \begin{array}{l} 34 \frac{35}{43} \\ 5 \frac{5}{77} \\ 40 \frac{40}{57} \\ 42 \frac{42}{44} \\ 38 \frac{38}{44} \end{array} \right.$	$\left\{ \begin{array}{l} 34 \frac{14}{42} \\ 29 \frac{29}{76} \\ 10 \frac{10}{58} \\ 7 \frac{7}{45} \end{array} \right.$	$\left\{ \begin{array}{l} 34 \frac{10}{42} \\ 34 \frac{34}{76} \\ 19 \frac{19}{58} \\ 57 \frac{57}{44} \end{array} \right.$
$\left\{ \begin{array}{l} do = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 69 \frac{51}{20} \\ 9 \frac{9}{9} \end{array} \right.$	$\left\{ \begin{array}{l} 70 \frac{13}{19} \\ 47 \frac{47}{19} \end{array} \right.$	$\left\{ \begin{array}{l} 70 \frac{36}{19} \\ 24 \frac{24}{19} \end{array} \right.$	$\left\{ \begin{array}{l} 70 \frac{24}{19} \\ 36 \frac{36}{19} \end{array} \right.$
$\left\{ \begin{array}{l} bo' = (010) : (111) \\ o's = (111) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 65 \frac{0}{24} \\ 51 \frac{51}{24} \end{array} \right.$	$\left\{ \begin{array}{l} 65 \frac{14}{24} \\ 46 \frac{46}{24} \end{array} \right.$	$\left\{ \begin{array}{l} 65 \frac{17}{24} \\ 48 \frac{48}{24} \end{array} \right.$	$\left\{ \begin{array}{l} 65 \frac{3}{24} \\ 57 \frac{57}{24} \end{array} \right.$
$\left\{ \begin{array}{l} eq = (101) : (011) \\ qp = (011) : (110) \\ ps = (110) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 38 \frac{27}{85} \\ 24 \frac{24}{56} \\ 9 \frac{9}{56} \end{array} \right.$	$\left\{ \begin{array}{l} 38 \frac{3}{86} \\ 28 \frac{28}{55} \\ 29 \frac{29}{55} \end{array} \right.$	$\left\{ \begin{array}{l} 37 \frac{46}{87} \\ 40 \frac{40}{54} \\ 34 \frac{34}{54} \end{array} \right.$	$\left\{ \begin{array}{l} 37 \frac{44}{87} \\ 22 \frac{22}{54} \\ 54 \frac{54}{54} \end{array} \right.$
$\left\{ \begin{array}{l} s'q = (101) : (011) \\ qp = (011) : (110) \\ ps' = (110) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 45 \frac{3}{64} \\ 0 \frac{0}{70} \\ 57 \frac{57}{70} \end{array} \right.$	$\left\{ \begin{array}{l} 45 \frac{9}{63} \\ 30 \frac{30}{71} \\ 21 \frac{21}{71} \end{array} \right.$	$\left\{ \begin{array}{l} 45 \frac{30}{62} \\ 55 \frac{55}{71} \\ 85 \frac{85}{71} \end{array} \right.$	$\left\{ \begin{array}{l} 45 \frac{21}{62} \\ 39 \frac{39}{72} \\ 0 \frac{0}{72} \end{array} \right.$
$\left\{ \begin{array}{l} r'o' = (201) : (111) \\ o'p = (111) : (110) \\ pr' = (110) : (201) \end{array} \right.$	$\left\{ \begin{array}{l} 34 \frac{35}{92} \\ 48 \frac{48}{52} \\ 37 \frac{37}{52} \end{array} \right.$	$\left\{ \begin{array}{l} 34 \frac{49}{92} \\ 40 \frac{40}{52} \\ 31 \frac{31}{52} \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{7}{92} \\ 40 \frac{40}{52} \\ 13 \frac{13}{52} \end{array} \right.$	$\left\{ \begin{array}{l} 35 \frac{17}{92} \\ 1 \frac{1}{52} \\ 42 \frac{42}{52} \end{array} \right.$

From the above comparative Table of 38 measured angles the salient fact is derived that the whole of the angles of the rubidium salt are intermediate between those of the potassium and caesium salts. The Table is best analysed in the following manner (as for former groups), by working out the average and maximum changes of angle for the various replacements:—

Replacement.	Average change. (Mean change of 38 angles.)	Maximum change.
K by Rb	25'	64' = 1° 4'
K by Cs	58'	136' = 2° 16'
K by NH <sub>4</sub>	49'	126' = 2° 6'

The average and maximum changes of angle are thus seen to be twice as great when potassium is replaced by caesium, as they are when potassium is replaced by rubidium, just as the change of atomic weight or atomic number is twice as great. So that the average change and the maximum change of interfacial angle are directly proportional to the change in atomic weight or atomic number.

The introduction of the radicle ammonium instead of potassium induces an amount of average or maximum change of angle which is just slightly less than when caesium is substituted for potassium. In the case of 35 of the angles the changes are in the same direction (of same sign) when ammonium is introduced for potassium, as when either rubidium or caesium is introduced, the only three exceptions being in cases where the change is very minute, not exceeding 6'.

It will be observed that the maximum change of angle for the whole group of four salts is  $2\frac{1}{4}^{\circ}$  ( $2^{\circ} 16'$ ), which occurs in the case of one angle,  $qp = (011) : (\bar{1}10)$ , when potassium in potassium cobalt selenate is replaced by caesium, or *vice versa*.

*Volume Constants.—*

Volume Constants of the Cobalt Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity	Molecular volume.	Topic axial ratios.
KCo selenate	527.77	2.530	208.60	$\begin{matrix} \times & \psi & \omega \\ 6.2197 : 8.2688 : 4.1856 \\ 6.2901 : 8.4693 : 4.2508 \\ 6.3618 : 8.7028 : 4.3418 \\ 6.3057 : 8.4651 : 4.2587 \end{matrix}$
RbCo        "        .....	619.87	2.837	218.49	
CsCo        "        ..	713.87	3.094	230.73	
NH <sub>4</sub> Co     "        .....	485.93	2.228	218.10	

The density increases with the molecular weight, the changes for the respective replacements of K by Rb and Rb by Cs being as 6:5, the effect thus diminishing as the mass grows. The ammonium salt is naturally much the lightest member of the group.

The molecular volume of the three alkali metallic salts increases at an accelerating rate, as the atomic weight or atomic number rises, the amount for the two changes of metal being 9.89 and 12.24 respectively. The molecular volume of ammonium cobalt selenate is almost identical with that of rubidium cobalt selenate, a result as regards the ammonium and rubidium salts always observed so far throughout the series.

The molecular volumes of the double selenates are naturally greater than those of the double sulphates, sulphur and selenium being analogues separated by two whole series of elements in the periodic table, their atomic numbers being 16 and 34; and it is interesting to see what is the amount

of the increase in the molecular volume on replacing sulphur by selenium. As there are two atoms of sulphur or selenium in the molecule of the double salt, we obtain the increase *per* atom by subtracting the molecular volume of the double sulphate from that of the double selenate and dividing by two. The results of doing this, for the analogous salts of all the five pairs of groups of monoclinic double salts yet completely investigated, are given in the next Table. The results also for the simple sulphates and selenates are added for comparison, and in this case, as there is only one atom of sulphur or selenium in the simple rhombic salt, there is no division by two, the differences of molecular volume for the analogous sulphate and selenate giving the increase *per* atom directly. Only the strictly analogous potassium, rubidium, and cesium salts are compared throughout; for no comparable value can be got for the simple ammonium salts, as ammonium selenate crystals are only available for molecular volume determinations in the monoclinic and not the rhombic form.

Increase of Molecular Volume on Replacing S by Se.

Salt group.	Increase per atom.
Cobalt	6.3 to 6.7 units
Iron	6.2
Nickel	6.1 to 6.8 "
Magnesium	6.0 to 6.1 "
Zinc ...	6.3 to 6.4 "
Simple salts of alkalis	6.5 to 6.8 "

The replacement of one atom of sulphur by an atom of selenium is thus found to be accompanied by an increase of 6.0 to 6.8 units of molecular volume. The results are very similar and concordant for the various groups of salts, both double and single.

The molecular distance (topic axial) ratios of the rubidium salt are also intermediate between those for the potassium and cesium salts, the axial or edge dimensions of the monoclinic elementary cell of the space-lattice increasing progressively with the atomic weight or atomic number of the alkali metal. These constants for the ammonium salt are almost identical with those for the rubidium salt, two of the three dimensions being very slightly greater, and the third a minute amount less. The space-lattice cells of the rubidium and ammonium salts are thus practically congruent or coincident.

*Cleavage.*—There is a perfect cleavage parallel to the orthopinakoid  $r'\{201\}$  in the crystals of all four salts. This is the common cleavage direction of the whole series of double sulphates, and of all the groups of the double

selenates yet studied, belonging to this same monoclinic isomorphous series crystallising with  $6H_2O$ . In addition, a feeble facility for cleavage has also been observed in ammonium cobalt selenate parallel to the clinopinakoid  $b\{010\}$ . Ammonium nickel selenate was also found to exhibit this same second cleavage direction, as also four of the ammonium double sulphates, those of the magnesium, nickel, manganese, and copper groups.

*Orientation of Optical Ellipsoid.*—The symmetry requires only one of the three rectangular axes of the optical ellipsoid to be fixed, namely, that which is identical with the symmetry axis  $b$ . The two others, lying in the symmetry plane, may be anywhere in that plane consistent with their mutual rectangularity. They are not only differently situated for the different salts, but even for the same salt they are dispersed slightly for different wave-lengths of light.

The position of the ellipsoid is thus conveniently determined by giving the position for a specific wave-length of that one of the two latter axes which is not far removed from the vertical crystal axis  $c$ ; it is the  $\alpha$  axis of the indicatrix and the second median line for all four salts.

*Inclination of  $\alpha$  Axis of Indicatrix to Vertical Axis  $c$ , in front, for Na Light.*

$NH_4Co$ selenate	2° 23'
KCo            "	.   8 51'
RbCo           "	12 50'
CsCo           "	. 19 23'

The Table indicates that the ellipsoid is so situated that in the crystals of the ammonium salts its  $\alpha$  axis lies very near, and just in front of, the vertical crystal axis  $c$ . In the crystals of the salts containing the three alkali metals it is situated so that this axis  $\alpha$  is further and further removed from the vertical axis as the atomic weight or atomic number of the alkali metal increases. The ellipsoid thus rotates about the symmetry axis  $b$  when one alkali metal is exchanged for another, and progressively at an accelerating rate, following the ascending order of the atomic weights or atomic numbers of the interchanged metals. Its position for each of the four salts is graphically indicated in fig. 9, which shows the progression clearly.

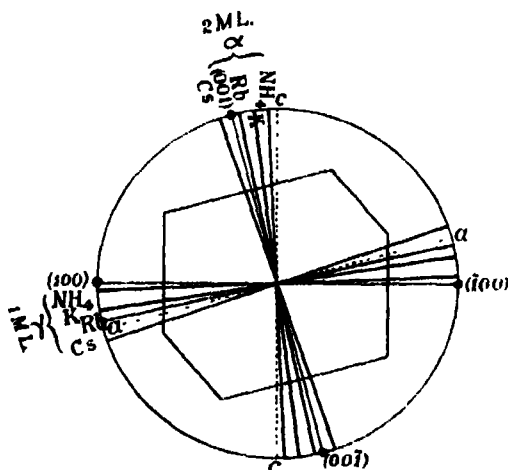


FIG. 9.

*Optic Axial Angles.*—The plane of symmetry  $b\{010\}$  is the common plane of the optic axes for the whole group. In all four cases the sign of the double refraction is positive, and the first median line is the  $\gamma$  axis of the indicatrix lying in the symmetry plane not far removed from the inclined crystal axis  $a$ .

Optic Axial Angles  $2V_a$  of the Cobalt Group of Double Selenates.

	KCo selenate.	RbCo selenate.	AmCo selenate	CsCo selenate.
Li . . . . .	62 12	73 42	82 5	87 11
O . . . . .	62 13	73 41	82 6	87 8
Na . . . . .	62 19	73 37	82 14	86 48
Tl . . . . .	62 27	73 33	82 22	86 32
Cd . . . . .	—	—	82 28	—

The optic axial angle is thus seen to increase with the atomic weight or atomic number of the alkali metal, the value for the rubidium salt being intermediate, slightly nearer to that of the potassium salt. The optic axial angle of ammonium cobalt selenate comes between those for the rubidium and caesium salts.

## Refractive Indices.—

Comparison of the Refractive Indices.

Index.	Light.	KCo selenate.	RbCo selenate.	NH <sub>4</sub> Co selenate.	CsCo selenate.
$\alpha$ .. .. .	Li ...	1.5122	1.5163	1.5223	1.5316
	C .....	1.5127	1.5168	1.5228	1.5321
	Na .....	1.5158	1.5199	1.5261	1.5354
	Tl .....	1.5190	1.5232	1.5294	1.5389
	Cd .....	1.5211	1.5252	1.5315	1.5409
	F .....	1.5231	1.5273	1.5335	1.5430
	G .....	1.5293	1.5333	1.5396	1.5492
$\beta$ .. .. .	Li .....	1.5181	1.5220	1.5287	1.5360
	C .....	1.5186	1.5225	1.5292	1.5365
	Na .....	1.5218	1.5256	1.5327	1.5399
	Tl .....	1.5250	1.5290	1.5362	1.5434
	Cd .....	1.5271	1.5311	1.5380	1.5454
	F .....	1.5291	1.5332	1.5401	1.5475
	G .....	1.5354	1.5393	1.5466	1.5539
$\gamma$ .. .. .	Li .....	1.5341	1.5329	1.5377	1.5412
	C .....	1.5347	1.5334	1.5382	1.5418
	Na .....	1.5390	1.5369	1.5417	1.5453
	Tl .....	1.5415	1.5404	1.5453	1.5489
	Cd .....	1.5435	1.5425	1.5474	1.5510
	F .....	1.5456	1.5446	1.5496	1.5531
	G .....	1.5522	1.5508	1.5562	1.5596
Mean refractive index $\frac{1}{3} (\alpha + \beta + \gamma)$ for Na light		1.5253	1.5275	1.5335	1.5402
Double refraction, $N_{\alpha} - \alpha$ .....		0.0222	0.0170	0.0156	0.0099

The  $\alpha$  and  $\beta$  indices of the rubidium salt will be observed to be intermediate between the corresponding indices for the potassium and caesium salts. As, however, a great diminution of double refraction ( $\gamma - \alpha$ ) for Na light occurs as the atomic weight or atomic number rises, the  $\gamma$  indices for the rubidium salt are slightly less than those of the potassium salt. The mean refractive index, however, for the rubidium salt is intermediate between the mean indices of the potassium and caesium salts. The effect of change of double refraction is overcome at the caesium salt, as the change in refractive index is a more considerably accelerating one, so that all the caesium salt indices indicate an advance in refractive power.

The refractive indices of the ammonium salt are intermediate between those of the rubidium and caesium salts.

*Double Refraction.*—The progression, a diminution, with rise in atomic number or atomic weight, already alluded to, will be clearly apparent from the last line of the Table. The value for the ammonium salt is just beyond that for the rubidium salt.

*Axial Ratios of Optical Indicatrix.*—Similar facts are expressed by these ratios of the axes of the indicatrix, which are directly proportional to the



refractive indices. The slight set-back of the  $\gamma$  value for the rubidium salt, due to the operation of the fall in double refraction, is shown by the second right-hand series of ratios, for all of which the  $\beta$  value of the potassium salt is taken as unity. This right-hand series of ratios expresses the total change in the dimensions of the optical ellipsoid on passing from one salt to the other, just as the Table for the inclination of the  $\alpha$  axis of the ellipsoid to the vertical crystal axis indicates the position of the ellipsoid in the various salts, the two Tables together thus giving complete information concerning the dimensions and orientation of the optical ellipsoid in the crystal.

### Axial Ratios of the Optical Indicatrix.

		$\alpha : \beta : \gamma$	$\alpha :$
KCo selenate	... ..	0.9960 : 1 : 1.0106	0.9960 : 1 : 1.0106
RbCo	"	0.9963 : 1 : 1.0074	0.9968 : 1.0025 : 1.0099
NH <sub>4</sub> Co	"	0.9957 : 1 : 1.0059	1.0028 : 1.007 : 1.0131
CsCo	"	0.9971 : 1 : 1.0035	1.0089 : 1.011 : 1.0154

### Molecular Optical Constants.—

#### Specific Refraction and Dispersion (Lorenz).

Selenate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ .						Specific dispersion. $n_a - n_c$ .		
	For ray C(Ha).			For ray H $\gamma$ near G.			$\alpha$ .	$\beta$ .	$\gamma$ .
	$\alpha$	$\beta$ .	$\gamma$ .	$\alpha$	$\beta$ .	$\gamma$ .			
AmCo	0.1371	0.1385	0.1404	0.1408	0.1423	0.1443	0.0037	0.0038	0.0039
KCo	0.1187	0.1199	0.1230	0.1220	0.1231	0.1263	0.0033	0.0032	0.0033
RbCo	0.1066	0.1076	0.1095	0.1094	0.1105	0.1124	0.0028	0.0029	0.0029
CsCo	0.1002	0.1009	0.1017	0.1028	0.1036	0.1044	0.0026	0.0027	0.0027

#### Molecular Refraction and Dispersion (Lorenz).

Selenate.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ .						Molecular dispersion. $m_a - m_c$ .		
	For ray C(Ha).			For ray H $\gamma$ near G.			$\alpha$ .	$\beta$ .	$\gamma$ .
	$\alpha$ .	$\beta$	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .			
KCo	62.86	63.27	64.91	64.86	64.98	66.68	1.70	1.71	1.77
RbCo	66.08	66.69	67.86	67.84	68.48	69.69	1.76	1.79	1.83
AmCo	66.60	67.28	68.24	68.41	69.12	70.13	1.81	1.84	1.89
CsCo	71.81	72.00	72.59	73.41	73.98	74.86	1.90	1.93	1.97

*The Transparency of Biotite to Infra-red Radiations.*

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(Communicated by Prof. H. L. Callendar, F.R.S. Received March 3, 1919.)

The important work of Sir W. Crookes on the infra-red transmission of certain glasses of definite composition was carried out largely with the help of black biotite, which mineral is, when in moderately thick sheets, quite opaque to light radiations, but is markedly transparent to the infra-red. For purposes of the comparison of certain results on commercial glare glasses obtained by the present writer with those given by Sir W. Crookes, it was desirable to determine exactly the transmission of biotite and its variation with wave-length.

A few rough results have been obtained by Koenigsberger,\* and are quoted by Coblenz, but evidently insufficient results were obtained to give exactly the true form of the transmission curve. Accordingly, the present work was designed to give as nearly as possible the variation of transmission in the most interesting points on the curve, especially near  $3\mu$ , where so many substances (especially those containing oxygen with hydrogen) show indications of or actual absorption bands. The singular temperature effect to be described was entirely an accidental discovery.

The apparatus employed was designed some ten years ago by Prof. Callendar (who kindly gave permission for its use) and Mr. A. Eagle. The arrangement of mirrors and prism is indicated in the diagram, fig. 1. The second mirror,  $M_2$ , can be rotated by a tangent screw action working at long radius, which was specially designed with a sleeve micrometer to indicate the inclination of the mirror. The angular motion corresponding to a turn of the screw head could be calculated from the dimensions of the apparatus.

The thermopile, T, is mounted behind the second slit,  $S_2$ , in the plane of which the spectrum is focussed. It is desirable of course to work with as small apertures as possible; in practice, the slits were approximately 1 mm. wide.

As spectrometric work in the infra-red is likely to receive increasing attention in future, it may not be out of place to examine simply the optical properties of the system which has been employed in this work. Firstly, it would be desirable that each mirror should be a *segment* of a paraboloidal

\* Koenigsberger, 'Ann. der Physik,' vol. 61, p. 687 (1897); Coblenz, Publ. 35, Carnegie Inst., Washington, 1905.

surface which has its apex in the line drawn through the desired focus parallel to the desired path of the parallel rays. Since, in practice, the mirrors cannot well fulfil this condition, spherical surfaces will be employed.

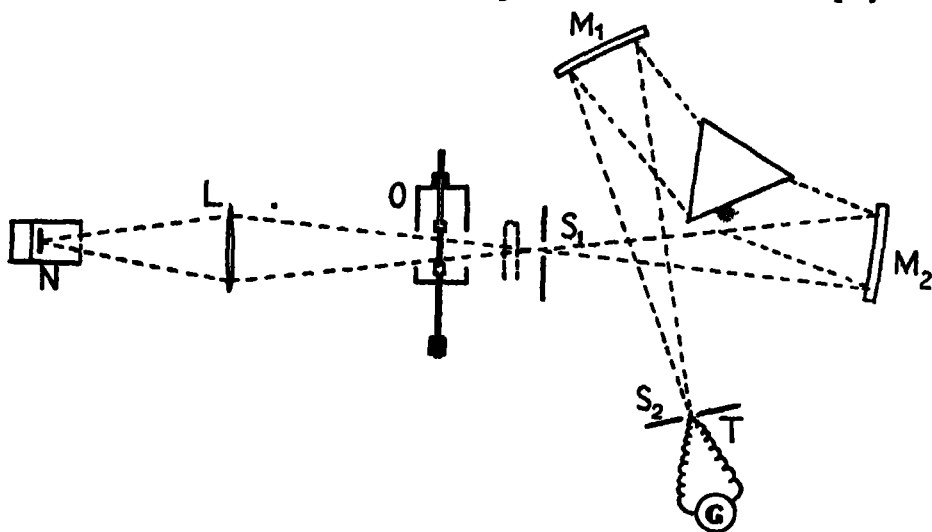
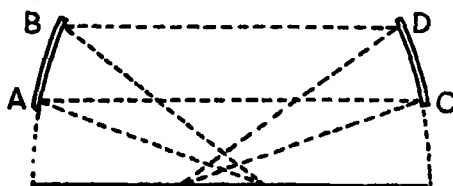


FIG. 1.

Under these circumstances, the centre of curvature (see fig. 2) of the surfaces will lie near the line mentioned above.



2a

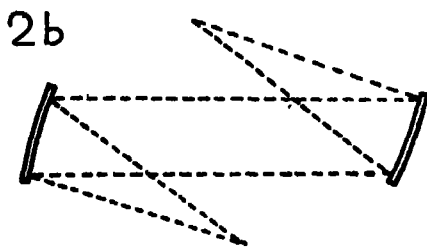


FIG. 2.

In fig. 2a the mirror system is shown, omitting the prism. If we now arrange the spherical surfaces so that they are tangential to the paraboloids

at A and C, we shall have true parallelism of the rays between A and C, but the aberrations at B and D will be in the same sense and will add together. This disadvantage can be overcome by arranging the mirrors as in fig. 2*b*—when the advantages of a symmetrical optical system are realised. The second arrangement, then, appears the best for general use, and it seems to have been adopted by most experimenters, but in actual practice it is found possible very largely to overcome any objectionable amount of coma by adjusting the focus of the instrument when using visible radiations. The reflected pencils are astigmatic, which for spectrometric work is a positive advantage when dealing with line spectra, but more especially in visual and photographic work, as “dust lines” in a narrow slit are not in focus.

In order to make sure that the amount of aberration present could not seriously interfere with the use of the apparatus, the width of the coma patch at the focus for the two extreme rays and a centre ray of an assumed parallel beam passing through the prism has been calculated for one mirror. Owing to the restricted size of the rock-salt prism the effective aperture of the mirrors was not greater than about 7 cm., and the angle of incidence of the principal centre rays was about 6°. The collimating mirror has a focal length of 100 cm., very nearly. The coma patch is represented by the distance, AB, from the centre principal ray to the intersection of the two extreme rays, see fig. 3*a*, and is a well-known criterion of the amount of coma present. This is easily calculated trigonometrically for the collimating mirror under the assumptions given above, and the magnitude of AB proves to be just under 0.01 cm.

Using a slit of negligible aperture, the coma present at the final focus of the apparatus is obviously of the order of double this amount, and may therefore be completely neglected in practice, especially as slits of at least 1 mm. had to be used for this infra-red work.

The following short geometrical discussion may possibly be helpful:—

Since the slit would be represented as at right angles to the diagram (fig. 3), we must deal with a “meridian” focus. Using the well-known formula for refraction of oblique meridian pencils at a curved surface

$$\frac{n' \cos^2 i'}{v} - \frac{n \cos^2 i}{u} = \frac{n' \cos i' - n \cos i}{r},$$

and adapting it to the case of reflection by putting  $n' = -n$  and  $i' = -i$ , the expression becomes

$$\frac{1}{v} + \frac{1}{u} = \frac{2}{r \cos i}.$$

If nearly parallel light passes through the prism in our apparatus, we have

that in general the distance from the point of incidence P to the meridian focus F, for parallel light  $PF_1 = \frac{r}{2} \cdot \cos i$ .

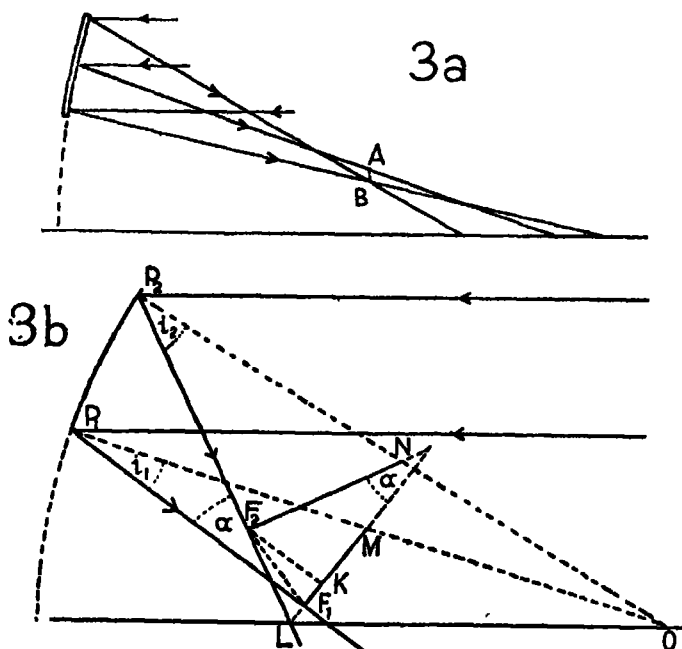


FIG. 3.

The geometrical meaning of this is seen clearly by drawing the radii  $OP_1$ ,  $OP_2$ , fig. 3b, bisecting them in M and N, and dropping perpendiculars ( $MF_1$ ,  $NF_2$ ) to the corresponding reflected rays. These points,  $F_1$ ,  $F_2$ , are the meridian foci for parallel pencils incident at  $P_1$ ,  $P_2$  respectively. Producing the perpendiculars and drawing  $F_2K$  parallel to  $P_1F_1$ , we see that the distance,  $F_1F_2$ , between the two meridian foci for the margins of the mirrors has a value lying between  $F_2L$  and  $F_2K$  or between  $\frac{r}{2} \sin i_2 \sin \alpha$  and  $\frac{r}{2} \sin i_2 \tan \alpha$  where  $\alpha$  is the angle of convergence of the beam. For the collimating mirror approximate values are  $\frac{r}{2} = 100$  cm.,  $\alpha = \frac{7}{100}$ ,  $i = \frac{1}{10}$ . Hence the distance,  $F_1F_2 = 0.7$  cm. approximately, or 0.7 per cent. of the focal length.

The best focus will lie between  $F_1$  and  $F_2$ , when only small amounts of residual aberrations will be encountered.

The considerations then which would prohibit the use of such a system for ordinary optical purposes are seen to be of less importance when dealing with line spectra. The actual definition given by the system is surprisingly good.

as shown by a photograph of a part of the red end of the visible iron spectrum taken by mounting a photographic plate in the plane of the thermopile without the protecting slit.

With slits of finite aperture the observed curves will be slightly in error. Thus the slit before the thermopile occupies (when 1 mm. wide) just over 2' of arc. With the 60° rock-salt prism and the mirror of 60 inches focus, the length of spectrum, assuming this to be pure, received on the thermopile is given approximately by the following Table:—

Region.	Length of spectrum received on thermopile.	Region.	Length of spectrum received on thermopile.
$\mu$	$\mu$	$\mu$	$\mu$
0·6	0·004	1·8	0·14
0·8	0·02	2·0	0·16
1·0	0·03	2·5	0·17
1·2	0·04	3·0	0·19
1·4	0·08	3·5	0·16
1·6	0·11	4·0	0·14

With the first slit 1 mm. wide, and a collimating mirror of 1 metre focus, the slit image is 1·5 mm. in width.

Lord Rayleigh\* has shown that the observed curve is connected with the true by a double integration,

$$y' = \frac{1}{4hk} \int_{x-k}^{x+k} dk \left\{ \int_{x-k}^{x+k} y dh \right\},$$

where  $2h$  is the width of the slit before the thermopile,

$2k$      "     "     image of the first slit,

$y'$  is the observed ordinate and  $y$  the true ordinate.

This leads to the rule for the correction of the ordinate to the curve. Following this rule, we compute

$$\sqrt{(h^2 + k^2)} = \sqrt{(0·5^2 + 0·7^2)} = 0·8 \text{ mm.}$$

This, at the point of maximum curvature  $2·75 \mu$  in the curves subsequently given, represents  $0·15 \mu$ .

Drawing ordinates at this distance, we find that the correction is of the same order as the probable errors of observation and it is therefore omitted. The only effect of the finite slit widths will be slightly to mask the true shape of the curves at points of maximum curvature.

Spectrum lines in the visible region were first focussed on the second slit, being observed with a telescope by displacing the pile and substituting a

\* 'Phil. Mag.,' vol. 42, p. 443 (1871).

reflecting prism. The rotation to be given to the second mirror to bring any given wave-length on the slit could be calculated from Ruben's results on the refractive index of rock salt. In this way the wave-lengths  $3.0\mu$  and  $4.4\mu$  were found. Their exact position was determined by the use of the water absorption band in a plate of selenite  $0.25$  mm. thick, and the emission band at  $4.4\mu$  given by a Bunsen burner. The position of the water absorption band is uncertain and has been located by various experimenters at differing wave-lengths near  $3.0\mu$ , at which it has been assumed to lie for this calibration. A curve of correction was thus obtained and wave-lengths are located consistently to  $0.02\mu$ .

The whole apparatus is enclosed in a double-walled box to prevent temperature disturbances, and this was closed after the observations on the visible spectrum. In general, a fresh calibration had to be made each day as the adjustment is extremely sensitive. Also the temperature of the whole room was kept as constant as possible to prevent parasitic E.M.F.'s in the thermopile circuit.

The source of radiation for the work was a Nernst glower (N, see fig. 1), run from a spare set of accumulators. It was enclosed by a screen of mica (with a window of thin quartz) to prevent draughts. The image of the filament was focussed on the slit by a rock-salt lens, L. This arrangement was found extremely satisfactory, and with care, absorption measurements could be repeated to well within 1 per cent. The zero of the galvanometer was taken before and after each reading by placing a screen between the rock-salt lens and the first slit, as a screen immediately in front of the pile produces serious zero errors owing to slight temperature differences. Measurements of transmission can be made consistently to within 1 per cent. at a given wave-length.

In some of the earlier trials the image of the Nernst glower was focussed on the slit by a concave mirror of silvered glass. This was of large aperture, and it was found that the heating effect at the focus was considerable. On one occasion it was noticed, on placing a piece of biotite in front of the slit, that the galvanometer deflection rose at first beyond its steady value. This effect was at once traced to the heating of the biotite, as when this was cooled by blowing on it the galvanometer deflections could be increased. Ordinary Muscovite mica shows no trace of this effect. Dechant\* could detect no change in absorption with a rise in temperature of  $120^{\circ}\text{C}$ .

In order to investigate the phenomena more fully a small electrically heated oven (O, fig. 1), lined with asbestos and having small windows of Muscovite mica, was employed. The general arrangement is shown in fig. 4.

\* Dechant, 'Wien. k. Akad. Ber.,' vol. 111, Abth. 2 A, p. 206 (1902).

The biotite was held in a small frame carried on a rod by means of which it could be brought between the windows or pushed to one side. A mercury thermometer close to the biotite indicated the internal temperature. It is difficult to fix exactly the temperature of any specimen under the necessary conditions of experiment as the crystal must be perfectly free to transmit radiation and may not be immersed in a liquid bath, or even in steam, owing to the high absorption which these expedients would entail. The method adopted doubtless gives the temperature within a few degrees. The slight radiation which the heating of the oven sends into the instrument made no observable effect on the galvanometer. The mica windows, which are of course kept always between the source and slit, reflect a small proportion of the radiation, but not sufficient to reduce it inconveniently.

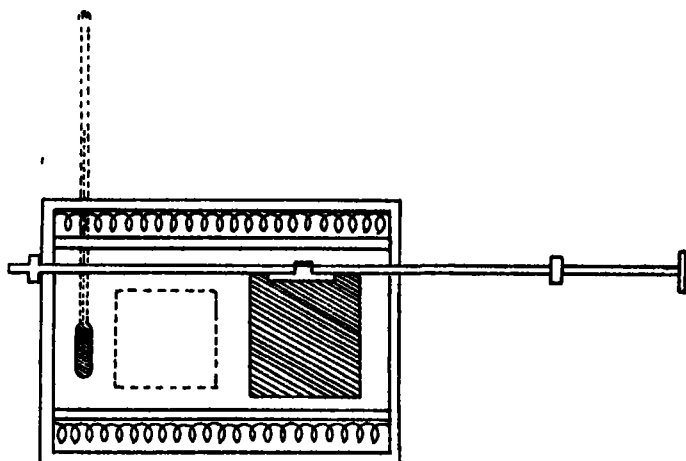


FIG. 4.

In making an experiment, the temperature was first allowed to become steady, small irregularities being controlled by a rheostat in the heating circuit. A series of absorption values was then taken for points between  $0.7\ \mu$  and  $4.5\ \mu$  (about), the observation extending over about two hours. Most of the work was done at night when experimental conditions are naturally of greater constancy.

Four specimens were exactly tested, two thicknesses from each of two varieties of biotite from differing localities. The actual transmission values obtained from each of the specimens are given.

In general, the effect of rising temperature is greatly to increase the absorption of the biotite; the transmission is halved at about  $200^{\circ}\text{C}$ . Although there are minor variations the effect is of the same order through the range of wave-length studied, i.e., from  $1.0\ \mu$  to  $4.5\ \mu$ .



Owing to war conditions only one galvanometer was available for the work, and this unfortunately was not sufficiently sensitive to enable the observations to be carried out far beyond  $4\mu$  (which is obviously extremely desirable and which will be done as soon as possible). Under the above circumstances the radiation of the Nernst glower was very weak at points beyond  $4\mu$  and the galvanometer deflections were very small. Results in this region must be taken with reserve.

Certain other results which appear to lie off the general track of the curves may be due to accidental temperature variations of the specimen.

Let  $I_0$  be the incident radiation, and let  $(1-\beta)$  be the transmission factor for a reflecting surface, also let  $\alpha$  be the "extinction coefficient," then very nearly

$$I_1 \text{ the transmitted radiation} = I_0(1-\beta)^2 10^{-\alpha t},$$

where  $t$  is the thickness of the medium.

For another thickness,  $t_1$ ,

$$I_2 = I_0(1-\beta)^2 10^{-\alpha t_1};$$

$$\text{then } \frac{I_2}{I_1} = 10^{\alpha(t-t_1)} \quad \text{and} \quad \log \frac{I_2}{I_1} = \alpha(t-t_1).$$

It should be noted that the formula given neglects the effect of multiple reflections. The reflection factor  $(1-\beta)$  is equal to  $\left\{1 - \left(\frac{n-1}{n+1}\right)^2\right\}$ , where  $n$  is the refractive index. It is assumed, as seems probable, that the refractive index will fall as is usual with increasing wave-length. There was, of course, no quasi-metallic reflection in the range of wave-length investigated.

Specimen No. 1 (thickness = 0.07 mm.).—Percentage Transmission and Temperature. See fig. 5.

Wave-length	187° C.	189° C.	73° C.	25° C.
$\mu$ .	per cent.	per cent.	per cent.	per cent.
0.90	—	—	—	6.9
1.43	—	—	24.9	26.5
1.66	23.5	28.1	45.2	47.3
2.47	63.7	68.2	70.2	73.7
2.78	66.6	68.8	—	—
3.68	66.2	68.9	72.5	73.0
3.97	64.8	68.9	72.9	74.2
3.40	75.4	77.8	79.8	80.7
3.66	77.2	79.2	—	—
3.68	76.8	79.3	80.7	80.4
3.87	78.2	78.9	—	—
4.12	78.6	77.6	72.0	74.6

Specimen No. 2 (thickness = 0.32 mm.). See fig. 5.

Wave-length.	187° C.	139° C.	132° C.	73° C.	25° C.
$\mu$ .	per cent.	per cent.	per cent.	per cent.	per cent.
1.43	0.2	0.2	0.2	0.5	—
1.66	1.1	1.5	1.7	2.6	—
1.8	2.3	4.6	5.2	7.9	—
2.06	9.7	18.8	16.8	23.2	—
2.47	18.3	26.9	28.0	36.8	42.6
2.78	23.6	30.9	34.4	42.0	—
2.88	23.3	30.0	33.9	39.4	43.8
2.97	25.0	32.3	34.9	40.4	45.6
3.07	31.4	36.5	42.3	45.9	52.9
3.16	35.0	42.4	44.5	52.1	—
3.40	41.0	47.6	51.7	59.4	61.4
3.56	47.6	52.3	56.3	62.3	63.7
3.68	47.7	52.8	57.5	62.1	63.9
3.87	48.3	53.6	57.6	60.9	62.2
4.18	42.0	51.8	55.0	—	55.7
4.54	36.4	41.7	—	42.1	40.8

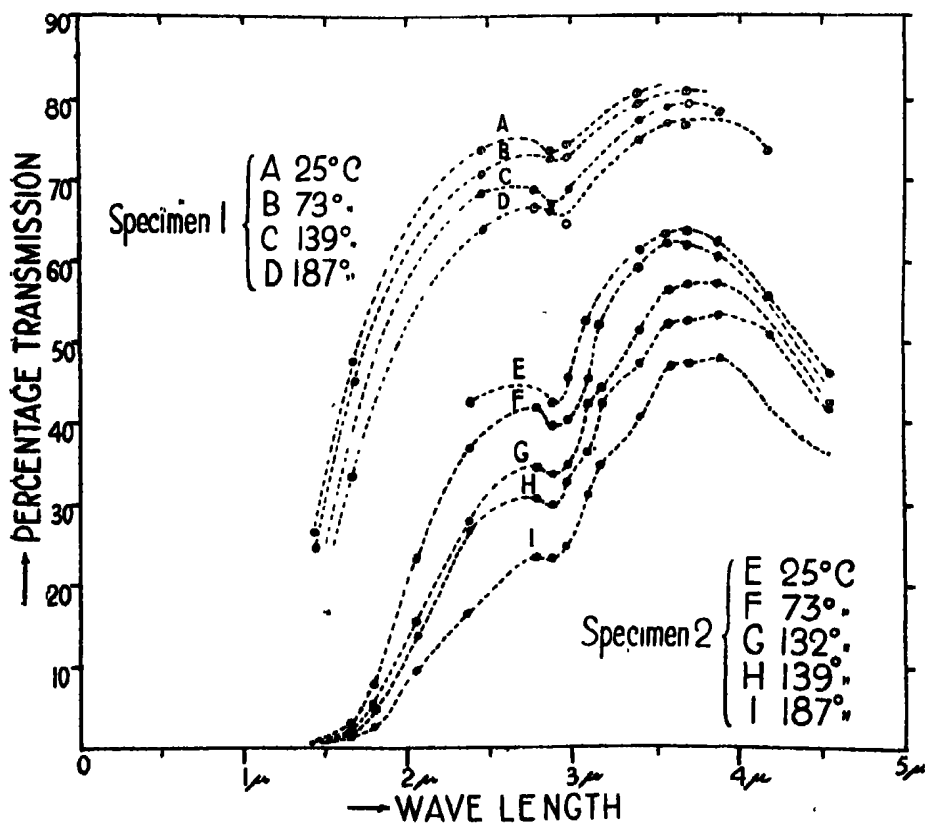


FIG. 5

The results given, although consistent, were obtained with somewhat inferior crystal plates. Later, through the kindness of Mr. Wiggins, I secured some excellent specimens from which perfect surfaces could be obtained. Two plates were selected of thickness 0.013 cm. and 0.035 cm., the measurements being obtained for calculation of the extinction coefficient. The following Tables give the results obtained for percentage transmission. Absorption values could be repeated from day to day with a consistency within 1 per cent., as has been already stated, but results taken at the same occasion with exactly the same adjustment are consistent to quite 0.2 per cent. in many cases. There are, of course, a certain number of somewhat doubtful individual results, as is inevitable in a long series of readings. Results given to 0.1 per cent. have thus a definite meaning in relation to *configuous values*, as is evident from their regularity.

Specimen No. 3 (thickness = 0.13 mm.). See fig. 6.

Wave-length.	Percentage transmission at 23° C.	Wave-length.	Percentage transmission at 23° C.
$\mu$ .		$\mu$ .	
0.71	1.05	3.0	72.6
1.33	4.29	3.0	74.2
1.52	17.2	3.12	77.1
1.82	47.5	3.22	77.5
2.25	66.4	3.65	80.4
2.76	70.7	3.85	77.1
2.88	68.2	4.06	77.5
2.91	68.2	4.24	73.8
2.96	71.0	4.44	62.6

Wave-length.	Percentage transmission at 250° C.	Wave-length.	Percentage transmission at 250° C.
$\mu$ .		$\mu$ .	
0.975	0.5	2.96	48.7
1.30	1.88	3.0	51.0
1.50	4.91	3.19	58.7
1.80	16.7	3.4	60.5
2.21	34.3	3.6	68.6
2.72	45.2	3.65	65.6
2.88	45.7	3.81	65.2
2.88	45.8	4.01	64.2
2.92	48.4	4.2	62.6

Specimen No. 4 (thickness = 0.35 mm.). See fig. 6.

Wave-length.	Percentage transmission at 25° C.	Percentage transmission at 110° C.	Wave-length.	Percentage transmission at 250° C.
$\mu$ .			$\mu$ .	
1.38	0.51	0.21	1.38	—
1.56	2.77	2.88	1.56	0.2
1.86	20.9	12.0	1.86	2.0
2.29	44.8	34.6	2.29	7.97
2.53	50.2	37.7	2.53	12.05
2.76	49.8	40.0	2.76	15.2
2.88	49.2	42.2	2.88	17.6
2.94	52.4	43.8	2.92	19.2
3.0	57.2	46.75	2.98	21.1
3.04	58.5	49.7	3.0	21.8
3.08	60.0	51.7	3.06	22.5
3.28	66.1	57.7	3.28	27.5
3.48	71.5	64.1	3.48	33.0
3.69	69.8	61.9	3.71	38.0
3.87	66.2	63.4	3.89	38.3
4.07	64.0	60.8	4.09	34.9
4.25	59.5	—	—	—
4.43	56.7	51.0	4.45	35.8

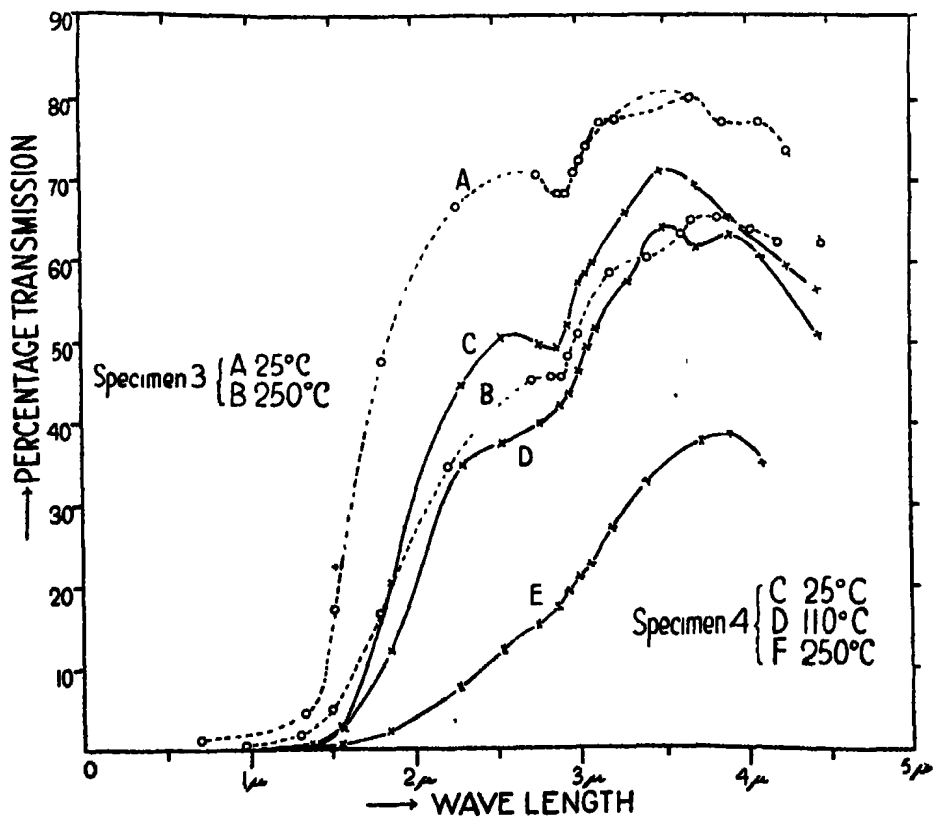


FIG. 6.

The temperature effect is reversible, and a few careful measurements were made on the same day with specimen No. 3, in order to detect any possible "hysteresis" or lagging effect. Absorption values were taken before and after prolonged heating at 250° C.

Wave-length.	Transmission before heating.	Transmission after heating.
$\mu$ .	per cent.	per cent.
2.83	69.5	69.7
3.6	80.6	79.5

Other measurements were also made on specimen No. 1 with similar results. No evidence of any lagging effect has been found.

From the transmission values of specimens Nos. 3 and 4, values for the extinction coefficient have been determined at 25° C. and 250° C. Results are tabulated below:—

Wave-length.	Extinction coefficient at 25° C.	Wave-length.	Extinction coefficient at 250° C.
$\mu$ .		$\mu$ .	
1.52	42.0	1.50	63
1.82	19.0	1.80	42
2.25	8.1	2.21	34
2.76	6.8	2.72	22
2.91	6.2	2.92	19
3.06	6.1	—	—
3.0	4.7	3.0	17
3.04	4.6	3.19	16
3.12	4.3	3.4	13
3.22	3.4	3.6	12
3.85	3.6	3.8	10
4.06	3.8	4.01	11
4.44	—		

From a first casual glance at the curves for No. 2 it would appear that rise of temperature acts simply as an increase of thickness, but on closer inspection important changes are noticed. The absorption band near 2.9  $\mu$  is seen to become much weaker with rising temperature. Further, the form of the curve between 3  $\mu$  and 4  $\mu$  alters considerably. It tends to flatten in the region of 3.4  $\mu$ , and the maximum transmission moves out to a greater wave-length. These results are borne out exactly by the curves for specimen No. 4, and as far as the apparatus is concerned, can doubtless be accepted as proved. The finite width of the slits used doubtless masks to some extent the true depth of the absorption band, but there can be no question of its disappearance in specimens Nos. 3 and 4 when the crystal is

heated to about 250° C. The curves appear to suggest that fresh absorption bands might be developed by a further rise of temperature.

In seeking to explain this temperature effect, several tentative suggestions presented themselves. Firstly, the effect might be due to a lamination of the crystals (as the result of increased temperature), which disappears on cooling. The result of this would be that the transmission curve at a higher temperature should be a replica of that at a lower (on a smaller scale), as a definite factor of increased reflection would come into play.

$$I, \text{ amount transmitted at higher temperature} = I_0(1-\beta)^n 10^{-at} \text{ (say),}$$

$$I_1, \quad \quad \quad \text{lower} \quad \quad \quad = I_0(1-\beta)^p 10^{-at},$$

then  $I/I_1 = \text{const.}$ , which is not the case.

Again, if the extinction coefficient increases regularly with temperature, the transmission at two temperatures  $\theta$  and  $\phi$  will be

$$I_\theta = I_0(1-\beta)^2 10^{-at},$$

$$I_\phi = I_0(1-\beta)^2 10^{-a[1+k(\phi-\theta)]t}, \text{ assuming a linear variation,}$$

$$\therefore \log \frac{I_\theta}{I_\phi} = atk(\phi-\theta), \text{ or } \log \frac{I_\theta}{I_\phi} = at(k \cdot \overline{\phi-\theta} + k_1 \cdot \overline{\phi-\theta}^2 + \text{etc.}, \text{ if the}$$

variation is not linear.

The log of the transmission ratios should be proportional to the extinction coefficient in either case throughout the range of wave-length if the constants  $k$ ,  $k_1$ , etc., keep the same values.

Wave-length.	Extinction coefficient.	Log $I_{250}/I_{25}$ .	Ratio.
$\mu$ .			
2.25	8.1	0.78	10.0
2.76	6.8	0.52	13.0
2.91	6.2	0.44	14.1
2.98	6.1	0.43	14.2
3.0	4.7	0.42	11.2
3.04	4.6	0.40	11.5
3.12	4.2	0.37	11.8
3.22	3.4	0.35	9.7
3.85	3.6	0.24	15.0
4.06	3.8	0.26	15.0

The values of the ratio  $I_{250}/I_{25}$  are found by interpolation on the curves for the wave-lengths at which the extinction coefficient is given, and, unfortunately, the coefficient itself is obtained partly from interpolated results; hence the Table given above must be taken as merely approximate. It shows that, roughly speaking, the magnitude of the variation is approximately the same over the range of wave-lengths investigated, but inspection

of the curves shows local differences which are unexplained by any simple law; this is supported by some consistency in the ratio variations of the extinction coefficient to  $\log I_0/I_1$  in the Table above.

Experiments were also made to determine the variation of transmission with temperature at a given wave-length. The following Table gives temperature and the corresponding transmission at  $\lambda = 2.29 \mu$ . (See fig. 7.)

Temperature.	Percentage transmission.	Log transmission.
° C.		
264	8.6	0.93
244	10.0	1.0
234	11.3	1.03
224	12.4	1.09
214	14.0	1.14
204	15.0	1.18
184	17.0	1.23
174	19.0	1.28
163	21.0	1.32
153	23.0	1.36
143	25.0	1.40
133	28.0	1.45
123	30.0	1.48
113	32.0	1.50
103	33.0	1.52
93	35.0	1.54
83	37.0	1.57
73	38.0	1.58

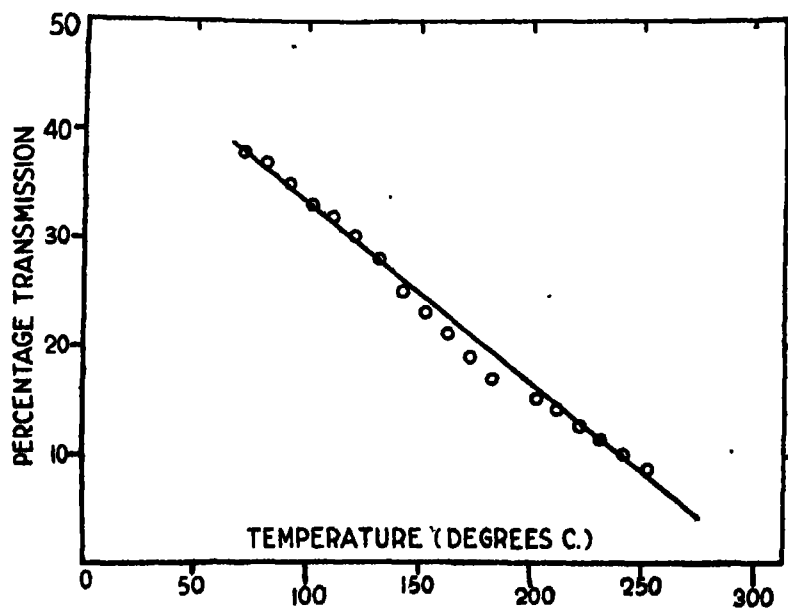


FIG. 7.—Percentage Transmission and Temperature at  $\lambda = 2.29 \mu$ .

The oven was heated up to about  $260^{\circ}$  C. and allowed slowly to cool, temperature and absorption values being taken regularly. The results appear to indicate an approximately linear variation of transmission with temperature at the wave-length of experiment; but the errors in temperature measurement may have somewhat affected the regularity of the figures.

Biotite is a mineral of somewhat variable composition, generally containing ferrous and ferric iron, magnesium, and aluminium as silicates with some hydrogen. It is found in widely separated localities, including Norway and East Africa, but the specimens on which the present work has been done are from British Columbia. Specimens from Norway and East Africa, and also a red variety from Ceylon, were tested with the heater, and found to exhibit the temperature effect in varying degrees, but exact measurements have not at present been made.

It will be remembered that the mineral has several curious properties. Its transmission of radiations vibrating perpendicular to the cleavage is enormously greater than the transmission of others vibrating parallel to the cleavage, or normally incident on the crystal face. No evidence has been found of a variation in the crystal axes with temperature which could explain the phenomenon.

The explanation of the infra-red transmission effect which has been described seems probably to lie in some temporary chemical change due to the rise of temperature. There is a great difference in the absorbing power of glasses containing ferrous and ferric iron. The diagram (fig. 8)

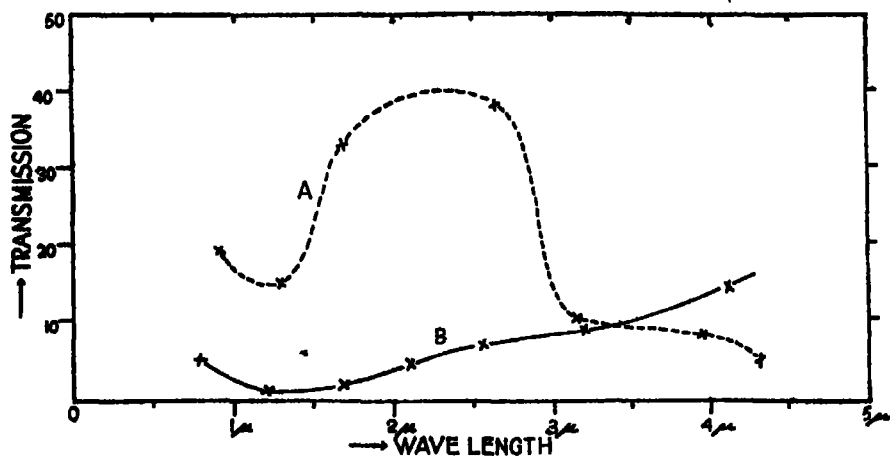


FIG. 8.

shows the percentage transmission of two specimens due to Sir W. Crookes—Nos. 202 and 246. The first, containing ferric iron and cobalt, is 2.89 mm.



thick, and the second, containing ferrous iron, is but 1.5 mm. The enormously greater absorption of the ferrous condition is shown. A regrouping of the elements forming the exceedingly complex molecule with a tendency towards the temporary formation of ferrous salts, would go far towards an explanation.

My best thanks are due to Prof. Callendar, F.R.S., Prof. Fowler, F.R.S., and Prof. Conrady, for their valuable advice in the preparation of the paper.

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*Experiments with Perforated Electrodes on the Nature of the  
Discharge in Gases at Low Pressures.*

By F. W. ASTON, M.A., D.Sc., Clerk-Maxwell Student of the University of  
Cambridge.

(Communicated by C. T. R. Wilson, F.R.S. Received May 22, 1919.)

In a paper on the influence of the nature of the cathode on the length of the Crookes' dark space\* some difficulties in the way of a satisfactory explanation of the mechanism of that phenomenon were indicated, which showed that it would be very advantageous to obtain, if possible, direct evidence as to how much of the total current passing through the discharge tube was brought up to the surface of the cathode by the positively charged ions falling upon it.

With a view to investigating this and some kindred problems, a discharge tube was made of the form indicated in section in fig. 1. It consisted of a cylindrical glass shade, closed at the lower end by stout glass plate, the electrodes being flat zinc discs just filling the tube. Zinc was used instead of aluminium as hitherto, as during the work with cathodes of different metals the former was found to give off very little gas and to sputter hardly at all, while the much greater ease with which it may be worked gives it a great advantage over the latter.

The upper electrode, A, was movable, being suspended by an improved form of the winch described in an earlier paper,† and which has now come into very general use in effecting accurate motion of objects within gas-tight apparatus.

\* F. W. A., 'Roy. Soc. Proc.,' A, vol. 87 (1912).

† 'Roy. Soc. Proc.,' A, vol. 84, p. 528 (1911).

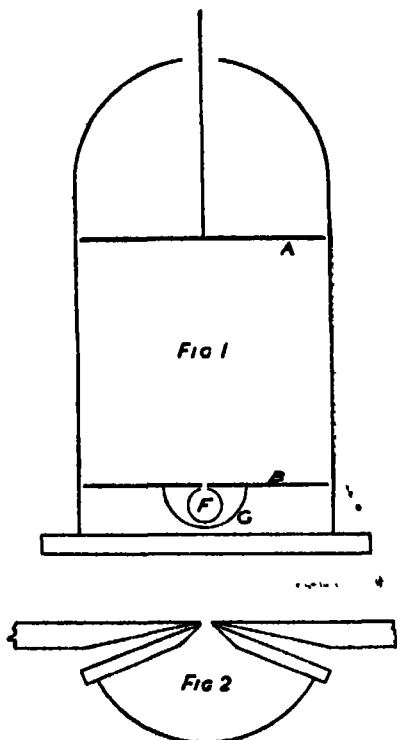
The lower fixed electrode, B, was perforated by a very narrow slit, shown in section in the figure, which extended almost the whole length of its diameter.

Behind this slit, and as close to it as possible, was a Faraday cylinder, F, made of a piece of brass tube closed at both ends and opened along its length by a parallel slit a little wider than the one in the electrode, fixed as indicated and insulated from the electrode by mica. This Faraday cylinder was protected from stray current from the gas in the space behind B by means of a guard tube, G, made of a half cylinder of brass closed at the ends, which completely enveloped it in a metal sheath kept at the same potential as B. Through a small hole in the guard tube an insulated lead from the Faraday cylinder was brought out through a nick in the edge of the shade, as also was a similar lead from the electrode itself.

The principal dimensions of the apparatus were as follows:—Diameter of electrodes, 11.8 cm.; area, 110 sq. cm. Length of slit, 10.0 cm. Mean width of slit, determined by measuring with a high power microscope at several points, 0.182 mm. Area, 0.182 sq. cm.  $1/605$  of the whole area of cathode.

In this apparatus the distance between the surface of the electrode and the edge of the Faraday cylinder was about 1.5 mm. This is of the order of the molecular mean free path at the pressures used, so, after some experiments had been done with it, as it was thought that so wide a gap might seriously affect the measurements of the current carried by the canaltrahlen into the Faraday cylinder, another apparatus was built, in which the special device indicated in fig. 2 is employed.

The lower electrode in this case was made of very stout zinc plate, the edges of the slit being chamfered off to a knife-edge as shown. The edges of the Faraday cylinder were also made of stout metal in the same way, so that it was possible to reduce the distance between the Faraday cylinder and the electrode to less than 0.1 mm.



The following were the dimensions of the second apparatus:—Diameter of electrodes, 11.5 cm.; area, 103.8 sq. cm. Length of slit, 9.50 cm.; area, 0.105 sq. cm. 1/989 total area of electrode.

As in the work on the dark space referred to (*loc. cit.*), the pressure in the tube was read by a McLeod gauge. The current in the main discharge tube was derived from a set of accumulators controlled by a water resistance, and measured with a Hartmann and Braun milliamperemeter suitably shunted to read in fifths of a milliampère.

It was found possible to turn the apparatus to several different uses. The following is an account of some of the experiments which were performed with it.

*Experiments to Determine the Relation between the Current entering the Faraday Cylinder and that in the Main Discharge Tube.*

In these experiments the lower electrode was made the cathode and connected to earth. The Faraday cylinder was connected to a sensitive Nalder D'Arsonval galvanometer, the other terminal of which was earthed. The galvanometer was carefully standardised, and the scale arranged to read exactly 10 divisions per microampère. As the resistance of the circuit was about 50 ohms and the maximum current 10 microampères, the difference between the potential of the Faraday cylinder and that of the cathode was never appreciable.

A large number of measurements were taken with oxygen in the first apparatus, and in the second with oxygen, atmospheric nitrogen and hydrogen, the usual procedure being to set the current at a definite series of values and read off that in the Faraday cylinder corresponding to each.

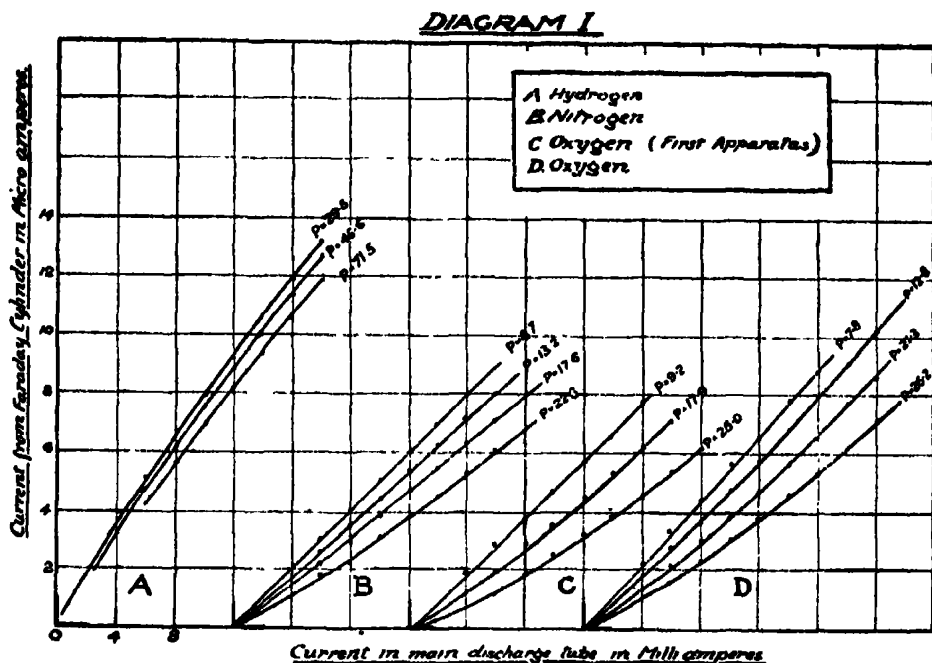
Diagram I shows some of the results so obtained, the current,  $i$ , flowing into the Faraday cylinder in microampères being plotted against the current  $c$  in the main discharge tube expressed in milliampères. In the set of curves, C, which were obtained with the first apparatus, the values of  $i$  have been multiplied by the fraction 605/989 so as to bring it into line with the other curves which were obtained with the second.

It will be seen that the curves obtained are not generally straight lines, although in the case of oxygen and nitrogen they tend to become so at low pressures, and that the curvature in the case of hydrogen is in the opposite sense to that in the other gases.

Unfortunately, on account of the very great practical difficulties involved in such a construction, the perforated electrode was not also made of the guard-ring type,\* so that at low pressures, or more strictly at pressures giving

\* F. W. A., 'Roy. Soc. Proc.' A, vol. 79, p. 86 (1907).

a long dark space, serious errors are made by the assumption that the current density on the surface of the cathode is measured by the total current passing through the tube. Too much importance must not be therefore attached to numerical results under such conditions.



It is particularly interesting to note that at high current densities (in hydrogen at all current densities) the slope of the curves does not alter very much with the pressure.

The following figures give, for currents of about 0.10 milliampère per square centimetre, the rate of change of current per unit area of the slit for a unit rate of change of current per unit area of the whole cathode. They therefore represent the fraction of such increase of current carried up to the cathode by the stream of positively charged particles if we suppose that all falling upon the area of the slit pass into the Faraday cylinder:—

Hydrogen .....	Pressure .....	71.5	45.3	36.8	29.5
	Fraction .....	0.63	0.63	0.64	0.64
Nitrogen .....	Pressure .....	22.8	17.6	13.2	8.7
	Fraction .....	0.40	0.43	0.45	0.50
Oxygen (1st app.) .....	Pressure .....	25.0	17.9	9.3	
	Fraction .....	0.40	0.46	0.48	
Oxygen (2nd app.) .....	Pressure .....	26.2	21.3	12.8	7.8
	Fraction .....	0.43	0.49	0.53	0.55

From these figures, it is evident that the great reduction in the dimensions of the slit and the gap between it and the Faraday cylinder has increased the fraction of the current in the latter only by 10 per cent. or so. From this it seems likely that the results with the latter apparatus are not very different from those which would be obtained with a theoretical apparatus in which these dimensions were infinitely small.

The results seem to indicate that *about half the current in the tube is brought up to the cathode by positively charged particles having sufficient velocity to get past the slit.* A very interesting conclusion but one which must be accepted with considerable caution in the light of results quoted below on the velocity of these particles.

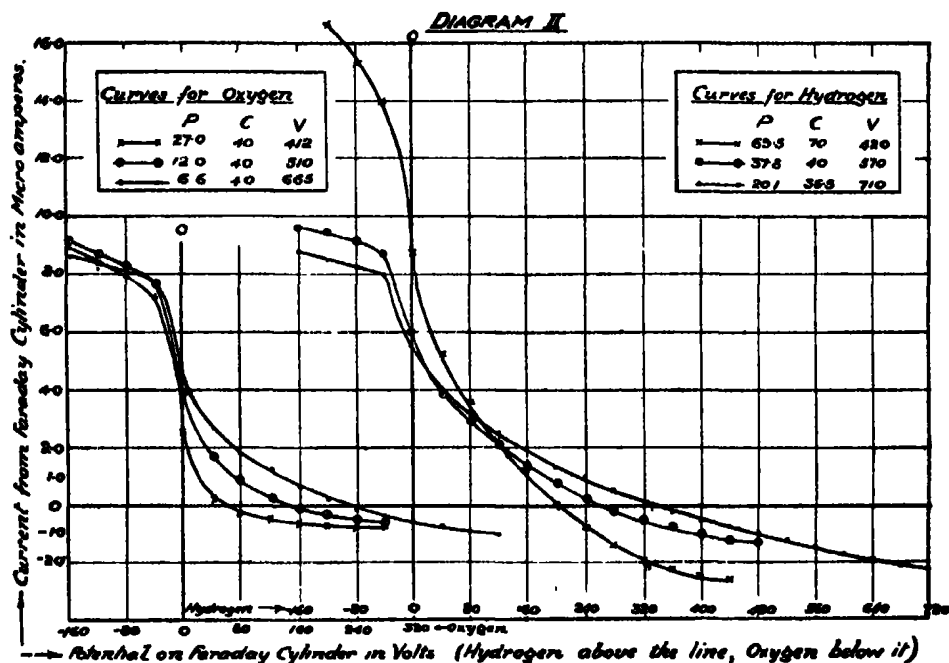
*Experiments to Investigate the Distribution of Velocity in the Stream of Positive Particles falling upon the Cathode.*

In these experiments, which were done with the second apparatus, the Faraday cylinder and its galvanometer were raised to different potentials with regard to the cathode. It was hoped that in this way, by plotting a curve at constant pressure and current, some knowledge might be gained as to the distribution of velocity among the positive carriers, as it is clear that, if the Faraday cylinder is raised to some definite potential,  $V$ , above the earthed cathode, only those carriers which have velocities greater than that obtained by falling through a potential,  $V$ , will get into it at all.

On Diagram II are shown the curves obtained by plotting the results of this investigation for hydrogen and oxygen, together with the values of pressure ( $P$ ), current ( $C$ ), and voltage ( $V$ ), in the main discharge tube for each curve.

It is very evident that accurate information on the point at issue is not directly obtainable in this way. In the first place, the current reaching the cylinder is actually reversed long before the value of  $V$  has risen as high as that between the electrodes. One explanation of this is to suppose that a strong current is derived from ionisation between the cathode and the edge of the cylinder; this would also account for the very rapid change of the value of the current on both sides of the value  $V = 0$ . If such an ionisation current originates entirely in the locality of the two slits, the ionisation intensity there must be far in excess of that one might be lead to infer from the consideration of the mean free path at the pressures employed. Also, it cannot be very well due entirely to the passage of normal positively charged canalstrahlen passing between the slits, for, in one of the experiments with hydrogen,  $V$  was increased up to the value of the potential between the

electrodes (a potential presumably sufficient to stop them completely), without the value of the negative current showing any signs of diminution.



There seems, however, another way of looking at the matter. This is to suppose a large number of the positively charged particles pick up, some one, some two, negative charges near the surface of the cathode. The former, now neutral and travelling with a high velocity, might help in the general ionisation, while the latter would carry a negative current into the cylinder, unless it was at a very large negative potential. With an increasing positive potential, on the other hand, none of the negative, but more and more of the positive, particles would be stopped, so that a reversal would take place, though it seems unlikely that it would be as great as is actually found.

From the general form of the curves, it seems probable that they represent the sum of several effects, which will be very difficult to separate from each other. For instance, the straight line obtained for high negative potentials, which grows steeper with increase of pressure, seems to indicate that, narrow as the slit in the cathode is, the cylinder is able to create an appreciable field on the other side of it, and so draw negative ions out of the intensely ionised region just in front of the cathode surface.

*Experiments with the Perforated Electrode as Anode.*

By reversing the battery and reading instruments, and so turning the lower disc into an anode, it was possible to investigate the current carried by the stream of cathode rays from the upper electrode, now the cathode, into the Faraday cylinder. By raising or lowering the cathode, different parts of the discharge could be examined.

The measurements obtained in the negative glow were particularly interesting. In this region it was found, using a constant current discharge, that *as the distance from the cathode is increased arithmetically, the current carried by the cathode rays into the Faraday cylinder decreases geometrically.*

At the edge of the dark space, the current density over the area of the slit appeared equal to that over the cathode itself, at low pressures even considerably greater. The latter inconsistency is probably due to the fact already referred to, that the value of the current density obtained from the total current is not reliable under those conditions, and gives readings too low by just about enough to account for it.

It seems, therefore, fairly certain that, at a point in the negative glow just beyond the dark space, practically the whole current is carried by the cathode rays, and that these rays are absorbed exponentially as they pass through the gas.

On Diagram III, the logarithm of  $i$ , the current from the cylinder is plotted against the distance between the electrodes for different pressures in oxygen. The result is a series of straight lines, whose slopes appear to be a function of the pressure.

The equation connecting the values may thus be written

$$i = ri' \quad \text{or} \quad i' = e^{-ki},$$

where  $i'$  is the current carried through the slit at a point distant 1 cm. further from the cathode than that which gives a current  $i$ .

The following are values of  $r$  and  $k$  for different pressures:—

Pressure.....	22.0	16.0	14.2	13.4	9.1
$r =$	1.98	1.83	1.76	1.62	1.38
$k =$	1.62	1.70	1.74	1.82	1.98

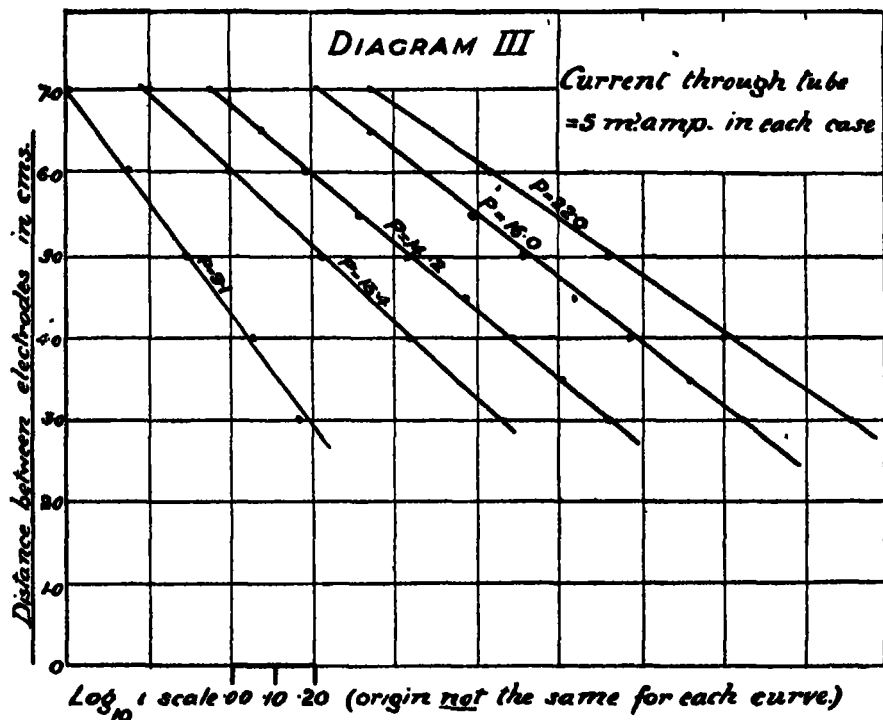
No very simple relation is apparent.

Two sets of readings were done in which  $L$  was fixed at 2.5 cm. and 5.0 cm. respectively, while the current through the discharge tube was varied. It was found that  $i$  increased rapidly with  $c$ , the relation being, very roughly,

$$c = ai^b - b,$$

$a$  and  $b$  being constants depending on  $L$ .

It seems probable that the determining value of  $L$  is not the distance between the slit and the cathode, but between the slit and the edge of the dark space, the latter value of  $L$  was not therefore constant in the second



set of readings, since the dark space alters in length with change of current density. Further experiments will be done on this point when opportunity occurs. The ones quoted above were made with the first apparatus.

#### *Experiments on the "Anode Glow."*

It has long been known\* that, using opposed electrodes not too far apart, when one increases the current the positive column shrinks as the negative glow stretches out from the cathode towards it, and finally disappears altogether.

With large plane parallel electrodes such as the author usually employed for work on the dark space the phenomena attending the disappearance of the positive column are very interesting.

In a gas like nitrogen the positive column shrinks very rapidly with increase of current until the last striation is left as a velvety glow on the

\* J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd ed., p. 554.



surface of the anode. This appearance, which will be referred to as the anode glow, now persists hardly altered through a considerable further increase of current, and finally, when the latter does reach a certain critical value, its disappearance takes place with surprising suddenness.

In 1906 when the conditions best suited for the measurement of the dark space were being examined it was noticed that the value of the critical current could be determined with considerable accuracy. The fact that in the second discharge tube, described above, the distance between the electrodes could be altered with great accuracy from 0 cm. to 20 cm. offered a very favourable opportunity for determining whether the disappearance of the anode glow was as definite a function of the distance from anode to cathode as it was of the current passing between them.

On trying the experiment remarkable results were obtained. In the discharge in pure atmospheric nitrogen at a pressure of about 0.15 mm., with a dark space of 1 cm., it was found that a movement of one of the electrodes of less than a millimetre was quite sufficient to determine the appearance or disappearance of the anode glow. And in general whatever the pressure and current, so long as they were constant, *the distance between the electrodes at which the anode glow just disappeared could be determined to within 1 per cent.*

A series of measurements were therefore carried out with nitrogen at various pressures, the procedure being as follows:—The current was set at a definite value. The upper electrode was then moved until the critical point was reached, it was then lowered a little to ensure complete disappearance. The current was now set exactly and the voltage read off. The upper electrode was then raised very carefully until the glow *just* reappeared, the distance between the electrodes was then read off on a millimetre scale.

When these results were plotted it was soon recognised that the important factors to be measured were the voltage and the distance between the anode and the edge of the dark space. A second series of experiments were done paying special attention to these, the results of which are plotted on Diagram IV.

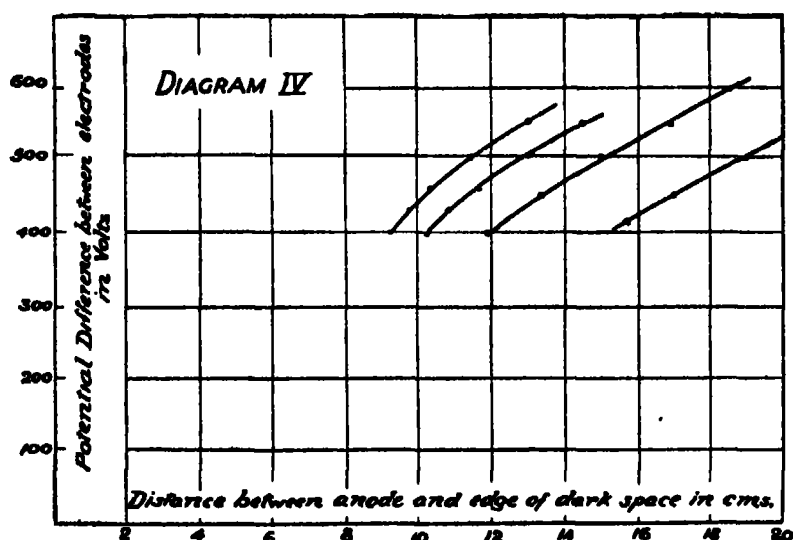
It will be seen that at constant pressure  $L$ , the distance between the anode and the edge of the dark space is a function of  $V$ , the potential difference between the electrodes (which has been already shown to be identical under these conditions to the fall of potential across the dark space)\* becoming almost linear at low pressures. And at constant  $V$  it is very nearly inversely proportional to the pressure.

\* 'Roy. Soc. Proc.,' A, vol. 84, p. 526 (1911).

The following are the values of L and P at constant potential of 500 volts:

P.....	21.0	18.4	15.7	11.9
L.....	11.4	13.0	15.0	19.0
$L \times P \dots$	240	240	236	229

If the lower perforated electrode is made the anode, the appearance of the glow is invariably attended by a sudden jump in the value of the negative current delivered into the Faraday cylinder. This is, indeed, a very delicate means of determining the critical point. The potential between the electrodes also always increases at the same time by a few volts.



The glow must be as intimately connected with the surface of the anode as it is with the distance from the cathode, for not only does it appear brighter on some parts of the anode than others, but also, once it has appeared, the distance between the electrodes can be increased enormously without altering any factor in the discharge appreciably.

The critical point would seem to be that at which the energy in the stream of cathode rays falls off to a definite minimum intensity. As this energy is almost certainly a function of both the potential and the current, the influence of these separately will have to be determined, *e.g.*, by the use of cathodes of various metals, before anything definite can be stated.

It is interesting to note that the spectrum of the anode glow is widely different from that of the negative glow in nitrogen, the former consisting entirely of bands, the latter largely of lines. Further experiments are projected on this phenomenon.

## 210 *On the Nature of Discharge in Gases at Low Pressures.*

In conclusion, I should like to express my thanks to Prof. Sir J. J. Thomson for the interest he has shown in these experiments.

### *Summary.*

Experiments are described on the discharge between electrodes of a large flat form perforated with a long narrow slit, the charge passing through the slit being collected and measured in a Faraday cylinder.

Direct measurements, made with the Faraday cylinder behind the cathode and at the same potential, seem to indicate that about half the total current in the discharge is brought up to the cathode by positive ions.

Attempts to discover the distribution of velocities in this stream show that this is not directly determinable, owing to the very high ionisation in the region of the slit and other reasons which are discussed.

Using a perforated anode, it is found that, as the distance from the cathode is increased arithmetically, the current carried by the cathode rays into the Faraday cylinder decreases geometrically when the current is constant.

The effect of (*a*) the distance apart of the electrodes and (*b*) the total current flowing, on the disappearance of the last trace of the positive column or anode glow, is shown to be remarkably definite, but no adequate explanation of this phenomenon seems available at present.

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*De Saint-Venant Solution for the Flexure of Cantilevers of Cross-section in the form of Complete and Curtate Circular Sectors, and on the Influence of the Manner of Fixing the Built-in End of the Cantilever on its Deflection.*

By MARY SEEGAR, B.Sc. and KARL PEARSON, F.R.S.

(Received May 24, 1919.)

(1) Hitherto, as far as we are aware, the well-known de Saint-Venant solution of the problem of flexure has been limited to a relatively few cases and in all these the cross-section of the beam possessed *biaxial* symmetry, there being an axis of symmetry in the plane of loading and also an axis perpendicular to this plane. De Saint-Venant's view that his solution could be directly applied to asymmetrical sections arises from a misconception. We have recently found it possible to extend the de Saint-Venant solution to certain cases in which there is only one axis of symmetry which may be (1) perpendicular to the plane of loading, or (2) in the plane of loading. The former case has been dealt with by Young, Elderton and Pearson in a memoir published last year.\* The flexure in this case is accompanied by torsion, and the problem is not without some bearing on the torsion of aircraft propeller blades, for which, indeed, it was worked out. The latter case for the same sections as were dealt with in that paper was then seen to be solvable, the axis of symmetry being now in and not perpendicular to the plane of loading. As far as we are aware no such cases of flexure with uni-axial symmetry of the cross-section have yet been published, although it is clear that a great variety of sections in actual use fall under this category.

For the particular section we have dealt with in this paper, that of a "trough" or "gutter-pipe" section, represented for mathematical purposes by a courtate circular annulus loaded in its plane of symmetry, we found it needful to introduce a term of the form  $C \log r$  in addition to the ordinary Fourier solution. We then obtained *two* equations for determining  $C$ , one from either curved surface of the annulus, and were checked in the course of our investigation. We are very grateful to Mr. W. M. Macaulay of King's College, Cambridge, for dispelling our difficulty by showing that the two equations could after some reduction be shown to be identical.

\* "On the Torsion resulting from Flexure in Prisms with Cross-sections of Uni-axial Symmetry only," 'Drapers' Company Research Memoirs,' Technical Series, No. VII, Cambridge University Press. On pp. 5 and 58 de Saint-Venant's misapprehension is discussed.

Following de Saint-Venant's admirable counsel that the mere algebraic solution of a problem was of little service until the physical meaning of it had been extracted by numerical reduction, we have applied very complicated formulæ to study more exactly than has hitherto been done the influence of the manner of fixing the terminal section of the cantilever on its droop. It is well known that the droop of a cantilever depends upon two factors: (*a*) the bending-moment deflection as provided by the old Euler-Bernoulli hypothesis, and (*b*) the shear deflection as developed in the more accurate de Saint-Venant theory. Unfortunately the shear deflection is largely dependent on the manner in which the terminal section of the cantilever is fixed. We have considered what proportion the shear deflection can bear to the bending-moment deflection according to the different methods of fixing which can be adopted within the restricted limits of de Saint-Venant's type of solution,

(2) We suppose a prism or cantilever clamped at one end and loaded perpendicularly to its axis at the other. To fix ideas let the axis be supposed that of  $z$  and horizontal, the axis of  $x$  be the direction of the load  $W$  and vertical, the axis of  $y$  be horizontal and perpendicular to the above. The origin is taken on the line of symmetry at a distance  $\bar{x}$  from the point where the line of centroids (prism axis) meets the fixed cross-section. The axis of symmetry of each cross-section will thus be the vertical. Let  $l$  be the length of the cantilever,  $I$  the principal moment of inertia of the cross-section about the horizontal axis in its plane. We will suppose the material isotropic,  $E$  being its stretch modulus and  $\eta$  its Poisson's ratio. We shall use the notation of the *History of Elasticity*, according to which the shifts are  $u, v, w$  parallel to the axes, the strains  $s_x, s_y, s_z, \sigma_{yz}, \sigma_{zx}, \sigma_{xy}$  and the stresses  $\widehat{xx}, \widehat{yy}, \widehat{zz}, \widehat{yz}, \widehat{zx}, \widehat{xy}$ . The de Saint-Venant hypothesis makes

$$\widehat{xx} = \widehat{yy} = \widehat{xy} = 0, \quad (i)$$

and leads, as it is easy to show, to:

$$\begin{aligned} u &= \frac{W}{EI} \left\{ \left( \frac{1}{2} \eta (x - \bar{x})^2 - y^2 \right) (l - z) + \frac{1}{2} l z^2 - \frac{1}{6} z^3 \right\} + \beta z + \alpha, \\ v &= \frac{W}{EI} \eta y (x - \bar{x}) (l - z), \\ w &= \chi(x, y) - \frac{W}{EI} \{ (x - \bar{x}) (l z - \frac{1}{2} z^2) + (x - \bar{x}) y^2 \} - \beta'' x + \gamma'', \end{aligned} \quad (ii)$$

where  $\frac{d^2 \chi}{dx^2} + \frac{d^2 \chi}{dy^2} = 0$ , and  $\beta, \alpha, \beta'', \gamma''$  are constants to be determined by the fixing.

The three stresses which are not zero are given by

$$\begin{aligned}\widehat{yz} &= \mu \left\{ \frac{d\chi}{dy} - \frac{W}{EI} (2 + \eta)(x - \bar{r}) y \right\}, \\ \widehat{zx} &= \mu \left\{ \frac{d\chi}{dx} - \frac{W}{EI} \left( \frac{1}{2} \eta \{ (x - \bar{r})^2 - y^2 \} + y^2 \right) + \beta - \beta'' \right\}, \\ \widehat{zz} &= -\frac{W}{I} (x - \bar{r}) (l - z),\end{aligned}\tag{iii}$$

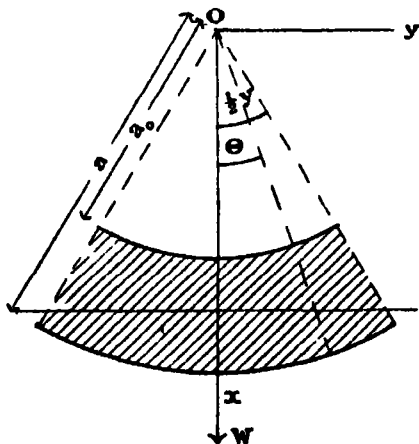
where  $\mu = \frac{1}{2} E / (1 + \eta)$  is the slide modulus.

Finally, the boundary condition is

$$\widehat{xz} dy - \widehat{yz} dx = 0.\tag{iv}$$

This is the most general form that can be given on the basis of de Saint-Venant's hypothesis to the solution for the flexure of a prismatic cantilever, when the cross-section is symmetrical with regard to the plane of loading.\*

(3) We propose to illustrate this solution in the case of a cantilever of which the cross-section is a curtate circular sector as shown in the accompanying diagram.  $\gamma$  is the sectorial angle; the co-ordinates of a point in the



section are  $r, \theta$  and the internal and external radii are  $a_0$  and  $a$  respectively. The equation for  $\chi$  will now be

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{d\chi}{dr} \right) + \frac{d^2 \chi}{r^2 d\theta^2} = 0,\tag{v}$$

\* See Pearson and Todhunter, 'History of Elasticity,' vol. II, pp. 56-8, and the memoir by Young, Elderton, and Pearson, above referred to, pp. 8-12.

A simple form of the solution of this equation is

$$\chi = C \log r + S \left( A_m r^m + \frac{B_m}{r^m} \right) \cos m\theta \\ + a_1 r \cos \theta + a_2 r^2 \cos 2\theta + a_3 r^3 \cos 3\theta, \quad (\text{vi})$$

where the terms in  $a_1, a_2, a_3$  are introduced to simplify the analysis.

We now turn to the boundary condition

$$\widehat{xz} dy - \widehat{yz} dx = 0,$$

which provides

$$\frac{d\chi}{dy} dx - \frac{d\chi}{dx} dy = \left[ -\frac{W}{EI} \left\{ \frac{1}{2} \eta ((z-\bar{x})^2 - y^2) + y^2 \right\} + \beta - \beta'' \right] dy \\ - \left[ -\frac{W}{EI} (2 + \eta) (x - \bar{x}) y \right] dx; \quad (\text{vii})$$

or, transforming to polars,

$$\frac{d\chi}{rd\theta} dr - \frac{d\chi}{dr} r d\theta = dr \left[ -\frac{W}{EI} \left\{ -r^2 (2 + \frac{1}{2} \eta) \sin \theta + 3r^2 \sin^3 \theta + 2\bar{x}r \sin \theta \cos \theta \right\} \right. \\ \left. + \left\{ -\frac{1}{2} \eta r^2 \frac{W}{EI} + \beta - \beta'' \right\} \sin \theta \right] \\ + r d\theta \left[ -\frac{W}{EI} \left\{ r^2 (3 + \frac{1}{2} \eta) \cos \theta - 3r^2 \cos^3 \theta \right. \right. \\ \left. \left. - \bar{x}r (\eta + 2 \sin^2 \theta) \right\} \right. \\ \left. + \left\{ -\frac{1}{2} \eta r^2 \frac{W}{EI} + \beta - \beta'' \right\} \cos \theta \right]. \quad (\text{viii})$$

Hence, converting the right-hand side into multiple angles, and remembering that either  $r$  or  $\theta$  is constant at the boundary, we have

$$\left( \frac{d\chi}{rd\theta} \right)_{\theta = \pm \frac{1}{2}\pi} = \left[ -\frac{W}{EI} \left\{ \left( \frac{1}{2} - \frac{1}{2} \eta \right) r^2 \sin \theta - \frac{3}{2} r^2 \sin 3\theta + \bar{x}r \sin 2\theta \right\} \right. \\ \left. + \left\{ -\frac{1}{2} \eta r^2 \frac{W}{EI} + \beta - \beta'' \right\} \sin \theta \right]_{\theta = \pm \frac{1}{2}\pi} \text{ for all values of } r, \quad (\text{ix}) \\ \left( \frac{d\chi}{dr} \right)_{r = \{a_0\}} = - \left[ \frac{W}{EI} \left\{ \left( \frac{3}{2} + \frac{1}{2} \eta \right) r^2 \cos \theta - \frac{3}{2} r^2 \cos 3\theta + \bar{x}r \cos 2\theta - \bar{x}r (1 + \eta) \right\} \right. \\ \left. + \left\{ -\frac{1}{2} \eta r^2 \frac{W}{EI} + \beta - \beta'' \right\} \cos \theta \right]_{r = \{a_0\}} \text{ for all values of } \theta. \quad (\text{x})$$

Substituting the value of  $\chi$  from (vi), the first equation gives us for both values of  $\theta$ :

$$-S \left( A_m r^{m-1} + \frac{B_m}{r^{m+1}} \right) m \sin \frac{1}{2} m\gamma - a_1 \sin \frac{1}{2} \gamma - 2a_2 r \sin \gamma - 3a_3 r^2 \sin \frac{3}{2} \gamma \\ = \left\{ -\frac{1}{2} \eta r^2 \frac{W}{EI} + \beta - \beta'' \right\} \sin \frac{1}{2} \gamma - \frac{W}{EI} \bar{x}r \sin \gamma \\ - r^2 \frac{W}{EI} \left\{ \left( \frac{1}{2} - \frac{1}{2} \eta \right) \sin \frac{1}{2} \gamma - \frac{3}{2} \sin \frac{3}{2} \gamma \right\},$$

and this will be satisfied identically if we take

$$\left. \begin{aligned} m &= 2i\pi/\gamma, i \text{ being an integer.} \\ a_1 &= \frac{W}{EI} \frac{1}{2} \eta \bar{x}^2 - (\beta - \beta''), \\ a_2 &= \frac{W}{EI} \frac{1}{2} \bar{x}, \\ a_3 &= -\frac{1}{3} \frac{W}{EI} \left\{ \frac{3}{4} - \left( \frac{1}{4} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{4} \gamma} \right\}. \end{aligned} \right\} \quad (\text{xi})$$

Thus we have

$$\begin{aligned} \chi &= C \log r + S \left( A_m r^m + \frac{B_m}{r^m} \right) \cos m\theta + \left\{ \frac{1}{2} \eta \bar{x}^2 \frac{W}{EI} - (\beta - \beta'') \right\} r \cos \theta \\ &\quad + \frac{1}{2} \bar{x} \frac{W}{EI} r^2 \cos 2\theta - \frac{W}{3EI} \left\{ \frac{3}{4} - \left( \frac{1}{4} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{4} \gamma} \right\} r^3 \cos 3\theta, \end{aligned} \quad (\text{xii})$$

where  $m = 2i\pi/\gamma$ .

We now substitute this value of  $\chi$  in (x) and find

$$\begin{aligned} S' \left( m \left( A_m a^{m-1} - \frac{B_m}{a^{m+1}} \right) \cos m\theta \right) &= -\frac{C'}{a} - \frac{W a \bar{x} (1 + \eta)}{EI} \\ &\quad + \frac{W a^2}{EI} \left\{ \left( \frac{3}{4} + \frac{1}{2} \eta \right) \cos \theta - \left( \frac{1}{4} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{4} \gamma} \cos 3\theta \right\}, \\ S \left( m \left( A_m a_0^{m-1} - \frac{B_m}{a_0^{m+1}} \right) \cos m\theta \right) &= -\frac{C}{a_0} - \frac{W a_0 \bar{x} (1 + \eta)}{EI} \\ &\quad + \frac{W a_0^2}{EI} \left\{ \left( \frac{3}{4} + \frac{1}{2} \eta \right) \cos \theta - \left( \frac{1}{4} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{4} \gamma} \cos 3\theta \right\}, \end{aligned} \quad (\text{xiii})$$

the range being from  $\theta = -\frac{1}{2}\gamma$  to  $+\frac{1}{2}\gamma$ .

Multiply both these equations by  $\cos m\theta$  and integrate throughout the range, we have

$$\begin{aligned} A_m a^{m-1} - \frac{B_m}{a^{m+1}} &= -(-1)^i \frac{\sin \frac{1}{2} \gamma}{\gamma} \left\{ \frac{3+2\eta}{m(m^2-1)} - \frac{3(1-2\eta)}{m(m^2-9)} \right\} \frac{W a^2}{EI}, \\ A_m a_0^{m-1} - \frac{B_m}{a_0^{m+1}} &= -(-1)^i \frac{\sin \frac{1}{2} \gamma}{\gamma} \left\{ \frac{3+2\eta}{m(m^2-1)} - \frac{3(1-2\eta)}{m(m^2-9)} \right\} \frac{W a_0^2}{EI}, \end{aligned}$$

leading to

$$\begin{aligned} A_m &= (-1)^i \frac{\sin \frac{1}{2} \gamma}{\gamma} \frac{a^{m+3} - a_0^{m+3}}{a^{2m} - a_0^{2m}} \left\{ -\frac{3+2\eta}{m(m^2-1)} + \frac{3(1-2\eta)}{m(m^2-9)} \right\} \frac{W}{EI}, \\ B_m &= -(-1)^i \frac{\sin \frac{1}{2} \gamma}{\gamma} \frac{a_0^{m+3} a^{m+3} (a^{m-3} - a_0^{m-3})}{a^{2m} - a_0^{2m}} \\ &\quad \left\{ -\frac{3+2\eta}{m(m^2-1)} + \frac{3(1-2\eta)}{m(m^2-9)} \right\} \frac{W}{EI}. \end{aligned} \quad (\text{xiv})$$



It now remains to determine C. Integrate the equations (xiii) between the limits  $-\frac{1}{2}\gamma$  and  $+\frac{1}{2}\gamma$  of  $\theta$ , and we find:

$$0 = \frac{C\gamma}{a} - \frac{W\alpha\bar{x}(1+\eta)}{EI}\gamma + \frac{Wa^2}{EI} \left\{ \left(\frac{3}{2}+\eta\right) \sin \frac{1}{2}\gamma - \frac{1}{2} \left(\frac{1}{2}-\eta\right) \sin \frac{1}{2}\gamma \right\},$$

$$0 = -\frac{C\gamma}{a} - \frac{Wa_0\bar{x}(1+\eta)}{EI}\gamma + \frac{Wa_0^2}{EI} \left\{ \left(\frac{3}{2}+\eta\right) \sin \frac{1}{2}\gamma - \frac{1}{2} \left(\frac{1}{2}-\eta\right) \sin \frac{1}{2}\gamma \right\}.$$

These equations at first appeared incompatible, but if  $\bar{x} = \frac{1}{3} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{a^3 - a_0^3}{a^2 - a_0^2}$  be inserted, we reach:

$$C = -\frac{1}{3} \frac{W(1+\eta)}{EI} \frac{a^2 a_0^2}{a+a_0} \frac{\sin \frac{1}{2}\gamma}{\gamma} \quad (\text{xv})$$

from both, a value absolutely symmetrical in  $a$  and  $a_0$ .

Thus we obtain the following value for  $\chi$ :

$$\begin{aligned} \chi = & \left\{ \frac{1}{2} \eta \bar{x}^2 \frac{W}{EI} - (\beta - \beta'') \right\} r \cos \theta + \frac{1}{2} \bar{x} \frac{W}{EI} r^2 \cos 2\theta \\ & - \frac{W}{3EI} \left\{ \frac{3}{2} - \left(\frac{1}{2} - \frac{1}{2}\eta\right) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \right\} r^3 \cos 3\theta - \frac{1}{3} \frac{W(1+\eta)}{EI} \frac{a^2 a_0^2}{a+a_0} \frac{\sin \frac{1}{2}\gamma}{\gamma} \log_e r \\ & + \sum_{n=1}^{\infty} (-1)^n \frac{\sin \frac{1}{2}\gamma}{\gamma} \left\{ -\frac{(3+2\eta)}{m(m^2-1)} + \frac{3(1-2\eta)}{m(m^2-9)} \right\} \frac{W}{EI} \times \\ & \left\{ \frac{a^{m+3} - a_0^{m+3}}{a^{2m} - a_0^{2m}} r^m - \frac{a^{m+3} a_0^{m+3} (a^{m-3} - a_0^{m-3})}{(a^{2m} - a_0^{2m}) r^m} \right\} \times \cos m\theta, \quad (\text{xvi}) \end{aligned}$$

where  $m = 2i\pi/\gamma$  and  $\bar{x} = \frac{1}{3} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{a^3 - a_0^3}{a^2 - a_0^2}$ .

If this value of  $\chi$  be inserted in equations (ii) and (iii) we have the full solution of the problem of flexure for a prism, the cross-section of which is a curtate circular sector, the load being in its plane of symmetry. It is, as far as we are aware, the first solution for flexure in the case of a section with uniaxial symmetry only, loaded in the direction of that axis. As the paper by Young, Elderton, and Pearson already referred to gives the solution for a prism of the same character loaded perpendicular to its plane of symmetry we have now the full solution for this case whatever be the plane of loading, i.e., the first de Saint-Venant flexure solution has been obtained when the direction of loading has no relation to any plane of symmetry at all.\*

The only constants that remain to be determined are the  $\alpha$ ,  $\beta$ ,  $\gamma''$  and  $\beta''$  of equation (ii). These depend upon the fixing of the "built-in" terminal section, and they provide the very limited variety of constraint which is

\* Of course de Saint-Venant's solutions for rectangle, ellipse, false ellipse, etc., admit of this extension, but being sections of bi-axial symmetry they do not involve either the associated flexural torsion or the presence of the logarithmic terms of this paper.

possible under the mathematical conditions of the de Saint-Venant problem and its solution.

It will be remembered that de Saint-Venant adopted as his fixing conditions (i) that the centroid of the terminal section should be fixed, *i.e.*,  $u = v = w = 0$  at that point, and also (ii) the direction of an elementary plane at that point should also be fixed, *i.e.*,  $dw/dr = 0$ . The conditions of the problem (see equation (ii)) make  $dv/dx = 0$  and  $du/dy = 0$  at the centroid also. We propose to compare this fixing in its influence on the deflection against that obtained by fixing more widely separated points of the terminal section, as far as such points can be fixed by the de Saint-Venant solution.

(4) We turn next to the value for the deflection. It is needful, however, to settle first what we mean by the "deflection." Turning to the first equation of (ii) we may take the shift at a point  $x_0$  on the axis of symmetry, *i.e.*,  $y = 0$ , at  $z$ ; this is

$$u_z = \frac{W}{EI} \left\{ \frac{1}{2} \eta (x_0 - \bar{x}) (l - z) + \frac{1}{2} lz^2 - \frac{1}{2} z^3 \right\} + \beta z + \alpha. \quad (\text{xvii})$$

Now, if  $f_{x_0}$  denote the difference between  $u_z$  and  $u_0$ ,

$$f_{x_0} = \frac{1}{2} \frac{Wl^3}{EI} + \beta l - \frac{\eta Wl}{2EI} (x_0 - \bar{x}). \quad (\text{xviii})$$

The simplest form, therefore, of the deflection will be obtained if we put  $x_0 = \bar{x}$ , and then

$$f_z = \frac{1}{2} \frac{Wl^3}{EI} + \beta l. \quad (\text{xix})$$

In this case  $\frac{1}{2} \frac{Wl^3}{EI}$  is the deflection  $f_1$  of the old Euler-Bernoulli theory, and is due to bending moment, while  $\beta l = f_2$  is the deflection added by the de Saint-Venant theory, and is the deflection due to shear. The ratio  $f_2/f_1$  is the ratio of these two deflections, and it is important to ascertain the extent to which this varies with (a) the nature of the "fixing" and (b) the nature of the cross-section, *i.e.*, in our particular case with the values of  $a_0$ ,  $a$ , and  $\gamma$ . But (xix) is not a good equation for experimental work, because the centroid of the "fixed" terminal will generally be inaccessible, and the centroid of the loaded section if accessible will often, as in trough or tubular sections, not be a physical point of the material of the cantilever itself. For experimental purposes it is almost essential to measure the droops of the cantilever from points of the mid-plane at top or bottom of the material of the cantilever, *i.e.*, where  $x_0 = a_0$  or  $a$ .

A good practical method is that applied in the memoir already cited:

$$\begin{aligned} u_z &= -\frac{Wl^3}{6EI} \left( \frac{z}{l} \right)^3 + \frac{Wl^3}{2EI} \left( \frac{z}{l} \right)^2 + \left( \beta l - \frac{\eta Wl}{2EI} (x_0 - \bar{x}) \right) \frac{z}{l} + \alpha + \frac{\eta Wl}{2EI} (x_0 - \bar{x}), \\ &= -a_3 \left( \frac{z}{l} \right)^3 + a_2 \left( \frac{z}{l} \right)^2 + a_1 \left( \frac{z}{l} \right) + a_0. \end{aligned}$$

Thus 
$$u_x - u_0 = -a_3 \left( \frac{z}{l} \right)^3 + a_2 \left( \frac{z}{l} \right)^2 + a_1 \left( \frac{z}{l} \right). \quad (\text{xx})$$

Now, measure  $u_x - u_0$  for a series of values of  $z/l$ , and find  $a_1, a_2, a_3$  by least squares, then  $2a_3$  will be the Euler-Bernoulli droop of the cantilever, and  $a_1$  will give the linear term or de Saint-Venant shear term by adding the correction  $\frac{1}{2} \frac{\eta W l}{EI} (x_0 - \bar{x})$ , which will be known as soon as we have chosen  $x_0$  the point for measurement of our deflections.

The ratio  $f_2/f_1$  will, of course, depend upon the ratio of (length of cantilever to linear dimension of cross-section)<sup>2</sup>, and will diminish as the length is increased.

The quantity  $W a^2/EI$  will frequently appear; let us call it  $q$ . Let  $I = \omega k^2$ , where  $\omega$  is the area of the cross-section, then  $W/\omega = L$  is the load per unit of area of cross-section, i.e., the mean shearing stress.  $k$  is the radius of gyration about the horizontal axis through the centroid and for the curtate sector, if  $u_0/u = \rho$ ,

$$\rho = \frac{l^2}{a^2} = \frac{1}{4} (1 + \rho^2) \left( 1 + \frac{\sin \gamma}{\gamma} \right) - \frac{16}{9} \frac{\sin^2 \frac{1}{2} \gamma}{\gamma^2} \left( 1 + \frac{\rho^2}{1 + \rho} \right)^2. \quad (\text{xxi})$$

Thus 
$$\frac{f_2}{f_1} = \beta \frac{W l^2}{3EI} = \frac{\beta}{q} \frac{3a^2}{l^2} = \frac{\beta}{qp} \frac{3k^2}{l^2},$$

where 
$$q = \frac{W a^2}{EI} = \frac{L}{Ep} = \frac{\zeta}{p}.$$

Hence, finally, 
$$\frac{f_2}{f_1} = \frac{\beta}{\zeta} \cdot \frac{3k^2}{l^2}. \quad (\text{xxii})$$

Here  $\zeta = L/E$  is independent of the form of the section, and the ratio  $\beta/q$  is what is most easily ascertainable from our formulæ. The value of  $q$  does not change with the nature of the fixing, nor the ratios  $k/l$  or  $a/l$ . Thus the ratio  $\beta/q$  is a good measure of how the shear term increases relative to the bending moment term with changes in the nature of the fixing.

(5) We will consider first the complete sector of sectorial angle  $\gamma$ , and will suppose, in de Saint-Venant's manner, an indefinitely small area fixed at the centroid,  $G$ , of the terminal section. Hence we must have  $u = v = w = 0$  when  $x = \bar{x}$ ,  $y = 0$ ,  $z = 0$ . These give us by (ii)

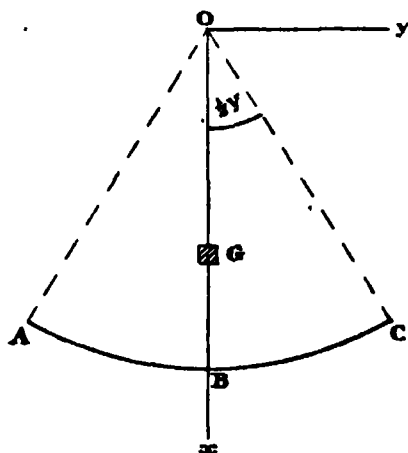
$$a = 0, \quad \chi(\bar{x}, 0) - \beta'' x + \gamma'' = 0, \quad (\text{xxiii})$$

and 
$$dw/dx = 0,$$

or 
$$0 = (d\chi/dx)_{(\bar{x}, 0)} - \beta''. \quad (\text{xxiv})$$

Equation (xxiv) will give  $\beta$ . Equation (xxiii) will then determine  $\gamma''$ , while

$\alpha = 0$ , and  $\beta''$  will disappear from the equations. We are,] therefore, practically only concerned with the determination of  $\beta$ .



Clearly only the  $A_m$  terms will occur in  $\chi$ , not the  $B_m$  terms, and  $(d\chi/dx)_{(x,0)}$  is  $(d\chi/dr)_{r=z, \theta=0}$ , and accordingly, from (xvi)

$$\beta'' = \frac{1}{2} \eta \left( \frac{\bar{r}}{a} \right)^2 \frac{W a^2}{EI} - (\beta - \beta'' + \left( \frac{\bar{r}}{a} \right)^2 \frac{W a^2}{EI} - \frac{W a^2}{EI} \left\{ \frac{1}{2} - \left( \frac{1}{2} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma} \right\} \left( \frac{\bar{r}}{a} \right)^2 + \sum_{i=1}^{\infty} (-1)^i \frac{\sin \frac{1}{2} \gamma}{\gamma} \left\{ -\frac{(3+2\gamma)}{m^2-1} + \frac{3(1-2\eta)}{m^2-9} \right\} \frac{W a^2}{EI} \left( \frac{\bar{r}}{a} \right)^{m-1} \Big\},$$

or, remembering that  $\bar{r} = \frac{1}{2} a \frac{\sin \frac{1}{2} \gamma}{\gamma}$ ,  $q = \frac{W a^2}{EI}$ , we have, re-arranging,

$$\frac{\beta}{q} = \left( \frac{4 \sin \frac{1}{2} \gamma}{3 \gamma} \right)^2 \left[ \frac{1}{2} + \frac{1}{2} \eta + \left( \frac{1}{2} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma} \right] + \frac{1}{2} \sum_{i=1}^{\infty} (-1)^i \left( \frac{4 \sin \frac{1}{2} \gamma}{3 \gamma} \right)^m \left[ \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \right], \quad (\text{xxv})$$

where  $m = 2\pi i/\gamma$ .

The series for  $\beta/q$  is always finite, except when  $m = 1$  or  $3$ , i.e.,  $\gamma = 2\pi$ ,  $\frac{2}{3}\pi$ , and  $\frac{4}{3}\pi$ , in which cases we have to proceed to certain limits.

(a.)  $\gamma = 2\pi$ . The terms of the series all vanish, because  $\sin \frac{1}{2} \gamma = 0$ , except the first and third. For these terms

$$\text{Limit}_{\gamma \rightarrow 2\pi} \left\{ \frac{1}{2} \left( \frac{4 \sin \frac{1}{2} \gamma}{3 \gamma} \right)^m \left[ \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \right] \right\}$$

has finite values  $= -\frac{1}{4}(3+2\eta)$  and  $0$ . Accordingly

$$\beta/q = 0.75 + 0.5\eta. \quad (\text{xxvi})$$

(b.)  $\gamma = \frac{2}{3}\pi$ , or  $m = 3i$ . Hence the first term of the series becomes infinite, but for this value of  $\gamma$  the term  $\sin \frac{1}{2} \gamma / \sin \frac{3}{2} \gamma$  also becomes infinite, and the two infinities are approached in the same way, and being of opposite sign, cancel. The method of obtaining the limit was to write  $m = 3(1+\epsilon)$ , and

expand in powers of  $\epsilon$ . Since  $m$  occurs in a power, a Napierian logarithm term arises in the limit.

$$\text{Limit}_{\epsilon \rightarrow 1} \left[ (-1)^i \frac{1}{4} \left( \frac{4 \sin \frac{1}{2} \gamma}{3\gamma} \right)^m \left\{ \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \right\} + \left( \frac{4 \sin \frac{1}{2} \gamma}{3\gamma} \right)^2 \left( \frac{1}{4} - \frac{1}{2} \eta \right) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma} \right]$$

is found to be, since the terms in  $1/\epsilon$  cancel:

$$\left( \frac{2 \sin \frac{1}{2} \pi}{\pi} \right)^3 \left( \frac{11+2\eta}{32} - \frac{3}{8} (1-2\eta) \log_e \frac{2 \sin \frac{1}{2} \pi}{\pi} \right).$$

Hence

$$\begin{aligned} \frac{\beta}{q} = & \frac{1}{4} (1+2\eta) \left( \frac{2 \sin \frac{1}{2} \pi}{\pi} \right)^2 + 2 \sum_{i=2}^{\infty} (-1)^i \left( \frac{2 \sin \frac{1}{2} \pi}{\pi} \right)^{2i} \frac{(1-\eta(3i^2-1))}{(i^2-1)(3i^2-1)} \\ & + \left( \frac{2 \sin \frac{1}{2} \pi}{\pi} \right)^3 \left( \frac{11+2\eta}{32} - \frac{3}{8} (1-2\eta) \log_e \frac{2 \sin \frac{1}{2} \pi}{\pi} \right). \quad (\text{xxvii}) \end{aligned}$$

(c.)  $\gamma = 4\pi/3$ , or  $m = 3i/2$ . The second term of the series now becomes infinite, but so also does the term in  $\sin \frac{1}{2} \gamma / \sin \frac{3}{2} \gamma$ , and proceeding as in (b), we have

$$\begin{aligned} \text{Limit}_{\epsilon \rightarrow 2} \left[ (-1)^i \frac{1}{4} \left( \frac{4 \sin \frac{1}{2} \gamma}{3\gamma} \right)^m \left\{ \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \right\} + \left( \frac{4 \sin \frac{1}{2} \gamma}{3\gamma} \right)^2 \frac{1-2\eta \sin \frac{1}{2} \gamma}{4 \sin \frac{3}{2} \gamma} \right] \\ = \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^3 \left\{ \frac{1-2\eta}{8} 3 \log_e \frac{\sin \frac{3}{2} \pi}{\pi} - \frac{11+2\eta}{32} \right\}. \end{aligned}$$

Hence

$$\begin{aligned} \frac{\beta}{q} = & \frac{1}{15} (4+\eta) \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^{3/2} + 8 \sum_{i=3}^{\infty} (-1)^i \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^{2i} \left\{ \frac{4-\eta(3i^2-4)}{(i^2-4)(9i^2-4)} \right\} \\ & + \frac{1}{4} (1+2\eta) \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^2 + \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^3 \left\{ \frac{3}{8} (1-2\eta) \log_e \frac{\sin \frac{3}{2} \pi}{\pi} - \frac{11+2\eta}{32} \right\}. \quad (\text{xxviii}) \end{aligned}$$

In the limiting case of  $\gamma = 0$  the series term will be found to vanish and  $\beta/q = 0.148148 + 0.148148\eta$ .

The following Table for  $\beta/q$  was then calculated from the above series, where  $\eta = 0.25$  gives this ratio for uniconstant isotropy:—

$\gamma$ .	$\beta/q$ .	$\beta/q$ for $\eta = 0.25$ .
0	$0.148148 + 0.148148 \eta$	0.1852
12	$0.148153 + 0.148517 \eta$	0.1848
30	$0.148338 + 0.187988 \eta$	0.1828
45	$0.149087 + 0.196944 \eta$	0.1808
60	$0.150718 + 0.115081 \eta$	0.1795
90	$0.187984 + 0.094726 \eta$	0.1816
120	$0.171537 + 0.082112 \eta$	0.1921
135	$0.180999 + 0.079086 \eta$	0.2008
180	$0.221608 + 0.085097 \eta$	0.2429
225	$0.298768 + 0.117675 \eta$	0.3132
240	$0.310197 + 0.135487 \eta$	0.3441
270	$0.378853 + 0.168157 \eta$	0.4191
315	$0.503000 + 0.291850 \eta$	0.5760
360	$0.750000 + 0.250000 \eta$	0.8125

The values are represented in the upper curve I of the accompanying Diagram I. It will be seen that, while the value falls from  $\gamma = 0^\circ$  to a

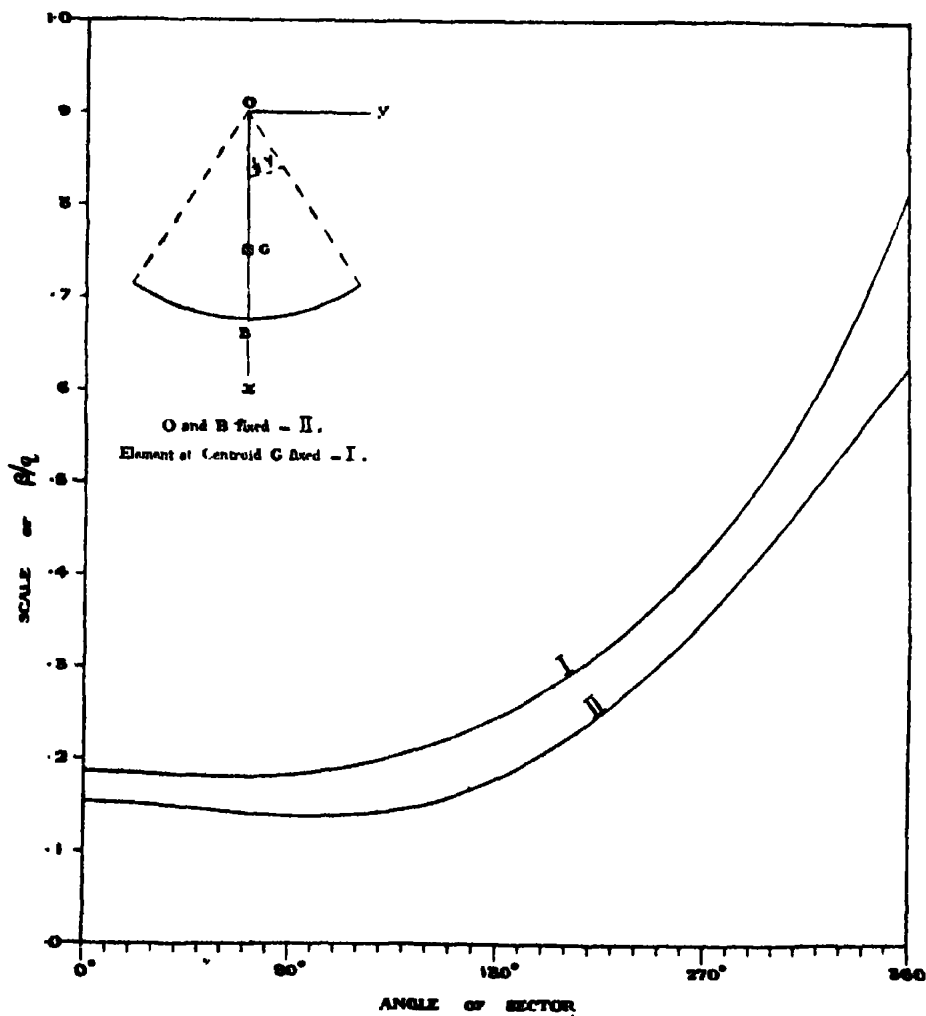


DIAGRAM I.—Non-curtate sectors. Fixing of de Saint-Venant centroidal element (I) and fixing of centre and lowest point of cross-section (II).

minimum at  $\gamma = 65^\circ.20$ , where  $\beta/q = 0.1794$  the fall is only slight; in fact, we may, for practical purposes, take  $\beta/q = 0.18$  for uniconstant isotropy for the first quadrant. After  $\gamma = 90^\circ$  the value rises continuously and fairly rapidly till it attains its maximum at  $\gamma = 360^\circ$ , which corresponds to a solid cylinder, with a slit in the plane of loading from periphery to axis. Sectorial prisms, with angles under  $12^\circ$ , may be looked upon as very closely

prisms whose sections are isosceles triangles, and in such cases the deflection due to shear is small compared to that due to bending moment. Thus, for a wedge-shaped cantilever, the length of which is not more than five times its depth, the shear deflection will only be about 2 per cent. of the bending moment deflection. In the case of the slit cylinder ( $\gamma = 360^\circ$ ), however, if the length be but five times the radius, the shear deflection is between 10 per cent. and 11 per cent. of the bending moment deflection; the length must be ten times the radius to reduce this to between 2 per cent. and 3 per cent.

(6) As the method of fixing suggested in the previous section is in practice impossible, we propose to vary it by fixing, as far as possible, the highest and lowest points of the central radius. If we fix the centre O, we have

$$u = v = w = 0 \text{ at } x = y = z = 0.$$

This leads to

$$\frac{1}{2}\eta \frac{W}{EI} \bar{x}^2 l + \alpha = 0, \quad \text{or} \quad \alpha = -\frac{1}{2}\eta \frac{W}{EI} \bar{x}^2 l,$$

$$\chi(0, 0) + \gamma'' = 0, \quad \text{or} \quad \gamma'' = -\chi(0, 0) = 0.$$

These equations can accordingly be satisfied by a proper choice of  $\alpha$  and  $\gamma''$ , and involve nothing further.

We now try to fix B by taking

$$u = v = w = 0, \text{ when } x = a, y = z = 0.$$

This leads to

$$\frac{1}{2}\eta \frac{W}{EI} (a - \bar{x})^2 l + \alpha = 0,$$

$$\chi(a, 0) + \gamma'' - \beta'' a = 0.$$

The first of these gives us  $\alpha = -\frac{1}{2}\eta \frac{W}{EI} (a - \bar{x})^2 l$ , which is incompatible with the previous value for  $\alpha$ , unless  $\bar{x} = \frac{1}{2}a$ . In this case we have

$$\frac{1}{2} = \frac{1}{2} \frac{\sin \frac{1}{2}\gamma}{\gamma}, \quad \text{or} \quad \frac{1}{2} = \frac{\sin \frac{1}{2}\gamma}{\frac{1}{2}\gamma},$$

which gives us

$$\gamma = 146^\circ 11' 4''$$

as the value of the sectorial angle for which we can fix both O and B. It is this sector which has its centroid at the midpoint of its axis of symmetry.

In the case of any other sector we can fix O, and fix B in the plane OAC, but B must have power of slipping along OB.

Assuming this condition satisfied, then since  $\gamma'' = 0$

$$\chi(a, 0) - \beta'' a = 0$$

will settle the value of  $\beta$ . It leads to

$$\frac{\beta}{q} = \sum_{i=1}^{\infty} (-1)^i \frac{\sin \frac{1}{2} i \gamma}{\gamma} \left\{ \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right\} + \frac{8}{3} \eta \left( \frac{\sin \frac{1}{2} \gamma}{\gamma} \right)^2 + \frac{1}{3} \frac{\sin \frac{1}{2} \gamma}{\gamma} - \frac{1}{12} (1-2\eta) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma}, \quad (\text{xxix})$$

where  $m = 2i\pi/\gamma$ .

Infinites arise, as in, the previous case, for  $\gamma = 2\pi, 4\pi/3$ , and  $2\pi/3$ , and we give briefly the results obtained by proceeding to the limits.

(a.)  $\gamma = 2\pi$ .

$$\text{Limit}_{i \rightarrow 1} (-1)^i \frac{\sin \frac{1}{2} i \gamma}{\gamma} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} = \frac{1}{4} (3+2\eta),$$

$$\text{Limit}_{i \rightarrow 3} (-1)^i \frac{\sin \frac{1}{2} i \gamma}{\gamma} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} = -\frac{1}{36} (1-2\eta).$$

And, accordingly,

$$\beta/q = 0.5 + 0.5\eta. \quad (\text{xxx})$$

(b.)  $\gamma = 4\pi/3$ . The second term of the series becomes infinite, and also the term in  $\sin \frac{1}{2} \gamma / \sin \frac{3}{2} \gamma$ .

$$\begin{aligned} \text{Limit}_{i \rightarrow 3} \left[ (-1)^i \frac{\sin \frac{1}{2} i \gamma}{\gamma} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} + \frac{1}{12} (1-2\eta) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma} \right] \\ = -\sin \frac{1}{2} \gamma \frac{(1-2\eta)}{16\pi} - \frac{\sin \frac{1}{2} \gamma}{\gamma} \frac{3+2\eta}{24} \\ = -\sin \frac{2\pi}{3} \frac{1}{32\pi} (5-2\eta) \end{aligned}$$

and accordingly,

$$\begin{aligned} \beta/q = \sum_{i=3}^{\infty} \frac{\sin \frac{1}{2} i \pi}{\pi} \frac{16(1-\eta(3i^2-4))}{3i(9i^2-4)(i^2-4)} + \frac{1}{2} \eta \left( \frac{\sin \frac{3}{2} \pi}{\pi} \right)^2 \\ - \frac{1}{4} + \left( \frac{11+2\eta}{32} + \frac{16(4+\eta)}{45} \right) \frac{\sin \frac{3}{2} \pi}{\pi}. \quad (\text{xxxi}) \end{aligned}$$

(c.)  $\gamma = 2\pi/3$ . The first term of series becomes infinite.

$$\begin{aligned} \text{Limit}_{i \rightarrow 1} (-1)^i \frac{\sin \frac{1}{2} i \gamma}{\gamma} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} + \frac{1}{12} (1-2\eta) \frac{\sin \frac{1}{2} \gamma}{\sin \frac{3}{2} \gamma} \\ = \frac{5-2\eta}{16\pi} \sin \frac{\pi}{3}. \end{aligned}$$

Hence

$$\begin{aligned} \beta/q = \frac{1}{3} \sum_{i=2}^{\infty} (-1)^i \frac{\sin \frac{1}{2} i \pi}{\pi} \frac{1-\eta(3i^2-1)}{i(9i^2-1)(i^2-1)} + 2\eta \left( \frac{\sin \frac{1}{2} \pi}{\pi} \right)^2 \\ - \frac{1}{4} + \frac{21-2\eta}{16} \frac{\sin \frac{1}{2} \pi}{\pi}. \quad (\text{xxxii}) \end{aligned}$$



From these formulæ the following Table of values for  $\beta/q$  was calculated:

$\gamma$ .	$\beta/q$ .	$\beta/q$ for $\eta = 0.25$ .
0	$\frac{1}{2} + \frac{1}{2}\eta$	0.1528
12	$0.110913 + 0.164000\eta$	0.1521
30	$0.109991 + 0.158365\eta$	0.1496
45	$0.108938 + 0.149800\eta$	0.1464
60	$0.108000 + 0.139697\eta$	0.1429
90	$0.108067 + 0.118585\eta$	0.1377
120	$0.113401 + 0.101889\eta$	0.1369
135	$0.118962 + 0.097078\eta$	0.1432
180	$0.160577 + 0.104009\eta$	0.1766
225	$0.207665 + 0.150880\eta$	0.2454
240	$0.232413 + 0.175828\eta$	0.2764
270	$0.289685 + 0.239158\eta$	0.3494
315	$0.390533 + 0.360915\eta$	0.4806
360	$0.500000 + 0.500000\eta$	0.6250

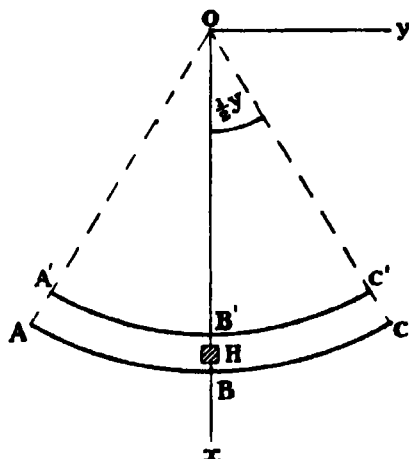
The values are plotted in the lower curve II of Diagram 1. It will be observed that for each sectorial angle the proportion of shearing deflection to bending moment deflection is less when we separate as far as possible the fixing points of the terminal section. In other words, de Saint-Venant fixing hypothesis tends to exaggerate the shearing deflection beyond what is likely to arise in any practical fixing, which must tend to fix points at a considerable distance from each other on the terminal section.

(7) We now turn to the annular sector which involves a number of interesting trough sections up to and including the tube with a longitudinal crack. Although the fundamental formulæ can be found for the value of  $\beta$  in special and general cases, the arithmetic is so laborious that we must content ourselves with a definite ratio of internal and external radii. We have taken the thickness,  $a - a_0$ , of the gutter or trough section to be one-tenth the external radius  $a$  or  $\rho = a_0/a = 0.9$ . The solution is there for any other ratio, but it would require the urgency of greater practical importance to work out a complete table of results corresponding to the double entry, *i.e.*,  $\rho$  as well as  $\gamma$ .

Let us first consider the de Saint-Venant method of fixing, *i.e.*, the fixing of a small element at the centroid as far as this is possible. This is theoretically possible as long as the centroid  $G$  remains within the area of the cross-section. But when  $G$  falls outside the curtate sector—for example, in the case of a semicircular gutter pipe, we could only fix  $G$  by attaching the non-material point rigidly by material to the cantilever. But it will then be the method by which this material attachment is made to the terminal section, and not any purely mathematical relations of the non-existent plane element at  $G$  which will determine the contribution of

shear to the droop. The values of  $\beta/q$  for the de Saint-Venant fixing would thus be purely mathematical and not practical as soon as the centroid with increasing sectorial angle passed outside the annular sector.\* To avoid this difficulty we have modified the de Saint-Venant's fixing, by fixing the elementary area not at the centroid, but at the midpoint, H, of the material in the axis of symmetry. Clearly  $OH = \frac{1}{2}(a + a_0) = \frac{1}{2}a(1 + \rho) = 0.95a$  for our special case.

If the "gutter pipe" has a relatively small thickness the fixing of the highest and lowest points of the actual material, *i.e.*, B and B', cannot give results differing widely from the fixing of the mid-elementary area, and it does not appear profitable for reasons just stated to fix any purely mathematical point. We have accordingly varied the nature of our fixing to one of a more practically realisable character in the following section. We



have fixed the lowest point B on the external boundary of the cross-section, and the highest points A', C' on the internal boundary of the cross-section, as far as this fixing is feasible. The result is of interest, for it indicates that to reduce the droop due to shear the fixing of the maximum number of points on the axis of symmetry is essential. The fixing of laterally situated points is not effective in diminishing shearing droop.

We now turn to the equations for fixing the element at H. We will take  $OH = \frac{1}{2}a(1 + \rho) = ap'$ , so that for our special numerical case  $\rho' = \frac{1}{2}(1 + \rho) = 0.95$ .

\* The condition for the centroid passing out of the cross-section is

$$\frac{\sin \frac{1}{2}\gamma}{\frac{1}{2}\gamma} = \frac{3}{2} \frac{\rho + \rho^2}{1 + \rho + \rho^2} \quad (\text{xxxi})$$

or, for our selected value of  $\rho = .9$ ,  $\frac{\sin \frac{1}{2}\gamma}{\frac{1}{2}\gamma} = .9464938$ , leading to  $\gamma = 65^\circ 25' 8''$ .

At H the de Saint-Venant "fixing" gives  $u = v = w = du/dx = 0$ , and accordingly, from equation (ii),

$$0 = \frac{1}{2}\eta \frac{W a^2 l}{EI} \left( \rho' - \frac{1}{2} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{1+\rho+\rho^2}{1+\rho} \right)^2 + \alpha,$$

which equation provides the value of  $\alpha$ , and

$$0 = \chi(\rho'a, 0) + \gamma'' - \rho'a\beta',$$

from which equation by (xvi)  $\beta''$  disappears, and the value of  $\gamma''$  is provided as soon as  $\beta$  is known.

Lastly: 
$$0 = \left( \frac{d\chi}{dr} \right)_{r=a} = \rho'a - \beta'',$$

from which equation  $\beta''$  again disappears, and we have the requisite relation to find  $\beta$ . Writing it out at length, we find:

$$\begin{aligned} \beta/q = & \frac{1}{2}\eta \left( \frac{1}{2} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{1+\rho+\rho^2}{1+\rho} \right)^2 + \rho' \frac{1}{2} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{1+\rho+\rho^2}{1+\rho} \\ & - \rho'^2 \left\{ \frac{1}{2} - \frac{1}{2}(1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \right\} - \frac{1}{2}(1+\eta) \left( \frac{\rho}{\rho'} \right)^2 \frac{\sin \frac{1}{2}\gamma}{\gamma} \\ & + \sum_1^{\infty} \left[ (-1)^i \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \frac{\rho'^{2m}-\rho^{2m}+\rho^{m+3}(1-\rho'^{2m})}{\rho'^{m+1}(1-\rho^{2m})} \right] \end{aligned}$$

where, as before,  $m = 2i\pi/\gamma$ .

(xxxiv)

As before, infinities arise when  $\gamma$  takes the values  $2\pi$ ,  $\frac{2}{3}\pi$ , and  $\frac{4}{3}\pi$ .

(a.)  $\gamma = 2\pi$ . All the terms of the series vanish except  $i = 1$ , and  $i = 3$ .

$$\begin{aligned} \text{Limit}_{i \rightarrow 1} \left[ (-1)^i \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \frac{\rho'^{2m}-\rho^{2m}+\rho^{m+3}(1-\rho'^{2m})}{\rho'^{m+1}(1-\rho^{2m})} \right] \\ = \frac{1}{4}(3+2\eta) \{1+\rho^2-(\rho/\rho')^2\}, \end{aligned}$$

$$\begin{aligned} \text{Limit}_{i \rightarrow 3} \left[ (-1)^i \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \frac{\rho'^{2m}-\rho^{2m}+\rho^{m+3}(1-\rho'^{2m})}{\rho'^{m+1}(1-\rho^{2m})} \right] \\ = -\frac{1}{12}(1-2\eta)\rho'^2. \end{aligned}$$

Hence 
$$\beta/q = \frac{1}{4}(3+2\eta)(1+\rho^2-\rho^2/\rho'^2) - \frac{1}{12}\rho'^2 \quad (\text{xxxv})$$

(b.)  $\gamma = \frac{2}{3}\pi$ . One infinity comes in with the term in  $\sin \frac{1}{2}\gamma/\sin \frac{3}{2}\gamma$ , and a second with the first term of the series. We have

$$\begin{aligned} \text{Limit}_{i \rightarrow 1} \left[ (-1)^i \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \frac{(\rho'^{2m}-\rho^{2m}+\rho^{m+3}(1-\rho'^{2m}))}{\rho'^{m+1}(1-\rho^{2m})} \right. \\ \left. + \rho'^2 \frac{1}{4}(1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \right] \\ = \frac{3}{4}\rho'^2 \frac{\sin \frac{1}{2}\pi}{\pi} \left\{ \frac{1}{12}(11+2\eta) - (1-2\eta) \left( \log_e \rho' - \frac{1-\rho'^2}{1-\rho^2} \frac{\rho^2}{\rho'^2} \log_e \rho \right) \right\}. \end{aligned}$$

And accordingly

$$\begin{aligned} \beta/q &= 2\eta \left[ \frac{\sin \frac{1}{2}\pi}{\pi} \left( 1 + \frac{\rho^2}{2\rho'} \right) \right]^2 - \frac{1}{2}\rho'^2 \\ &\quad + \frac{\sin \frac{1}{2}\pi}{\pi} \left\{ 2\rho' + \rho^2 + \frac{1}{16}(11+2\eta)\rho'^2 - (1+\eta)(\rho/\rho')^2 \right\} \\ &\quad - \frac{1}{2}(1-2\eta) \frac{\sin \frac{1}{2}\pi}{\pi} \rho'^2 \left\{ \log_e \rho' - \frac{1-\rho'^6}{1-\rho^6} (\rho/\rho')^6 \log_e \rho \right\} \\ &\quad + \frac{1}{2} \frac{\sin \frac{1}{2}\pi}{\pi} \sum_{i=2}^{\infty} (-1)^i \frac{1-\eta(3i^2-1)}{(i^2-1)(9i^2-1)} \frac{\rho'^{6i} - \rho^{6i} + \rho^{3i+3}(1-\rho'^{6i})}{\rho'^{3i+1}(1-\rho^{6i})}. \end{aligned} \quad (\text{xxxvi})$$

(c.)  $\gamma = 4\pi/3$ . One infinity comes in with the term in  $\sin \frac{1}{2}\gamma/\sin \frac{3}{2}\gamma$ , and a second with the second term of the series. Proceeding to the limit:

$$\begin{aligned} \text{Limit}_{i \rightarrow 2} &\left[ (-1)^i \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{24-8\eta(m^2-3)}{(m^2-1)(m^2-9)} \frac{\rho'^{2m} - \rho^{2m} + \rho^{m+3}(1-\rho'^{2m})}{\rho'^{m+1}(1-\rho^{2m})} \right. \\ &\quad \left. + \frac{1}{2}\rho'^2(1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \right] \\ &= \frac{1}{2}\rho'^2 \frac{\sin \frac{1}{2}\pi}{\pi} \left\{ -\frac{1}{16}(11+2\eta) + (1-2\eta) \left( \log_e \rho' - \frac{1-\rho'^6}{1-\rho^6} (\rho/\rho')^6 \log_e \rho \right) \right\}, \end{aligned}$$

and accordingly,

$$\begin{aligned} \beta/q &= 2\eta \left[ \frac{\sin \frac{3}{2}\pi}{2\pi} \left( 1 + \frac{\rho^2}{2\rho'} \right) \right]^2 - \frac{1}{2}\rho'^2 + \frac{\sin \frac{3}{2}\pi}{2\pi} [2\rho' + \rho^2 - \frac{1}{16}(11+2\eta)\rho'^2 \\ &\quad - (1+\eta)(\rho/\rho')^2] \\ &\quad + \frac{1}{2}(1-2\eta) \frac{\sin \frac{3}{2}\pi}{2\pi} \rho'^2 \left\{ \log_e \rho' - \frac{1-\rho'^6}{1-\rho^6} (\rho/\rho')^6 \log_e \rho \right\} \\ &\quad + \frac{1}{16} \frac{\sin \frac{3}{2}\pi}{2\pi} (4+\eta) \frac{\rho'^2(1+\rho \frac{3}{2}) - \rho^3(1-\rho'^3)}{\rho'^{4/3}(1+\rho^{3/2})} \\ &\quad + 16 \frac{\sin (2\pi/3)}{2\pi} \sum_{i=3}^{\infty} \left[ (-1)^i \frac{4-\eta(3i^2-4)}{(i^2-4)(9i^2-4)} \frac{\rho'^{3i} - \rho^{3i} + \rho^{i+3}(1-\rho'^{3i})}{\rho'^{i+1}(1-\rho^{3i})} \right]. \end{aligned} \quad (\text{xxxvii})$$

From formulæ (xxxiv)–(xxxvii) the following Table for  $\beta/q$  has been constructed. It indicates that the droop due to shear is greatest for the complete tube with a longitudinal slit along the top, but is never very significant, even for this case, amounting only to about 1.5 per cent., when the length of the tube is only five times its external radius. For semi-circular and flatter “gutter pipe” sections the shearing droop is negligible. This is, of course, on the assumption that a small element at the mid-point of the thickness in the median plane has been fixed in the de Saint-Venant manner. In the present illustration such a fixing can hardly differ practically from clamping the mid-thickness in a vice. The values of  $\beta/q$  are plotted as (I) in the accompanying Diagram II:—

$\gamma$ .	$\beta/\eta$ .	$\beta/\eta$ for $\eta = 0.25$ .
0	$0.002498 + 0.002498 \eta$	0.0031
12	$0.002501 + 0.000704 \eta$	0.0027
30	$0.002546 + 0.000108 \eta$	0.0028
45	$0.002616 + 0.000855 \eta$	0.0027
60	$0.002715 + 0.001089 \eta$	0.0030
90	$0.002968 + 0.004879 \eta$	0.0042
120	$0.003349 + 0.014288 \eta$	0.0069
135	$0.003619 + 0.021830 \eta$	0.0090
180	$0.004308 + 0.061219 \eta$	0.0196
225	$0.005141 + 0.129299 \eta$	0.0375
240	$0.005526 + 0.157970 \eta$	0.0450
270	$0.006011 + 0.224066 \eta$	0.0820
315	$0.006798 + 0.338411 \eta$	0.0914
360	$0.007495 + 0.456247 \eta$	0.1216

It will be seen that, up to the semicircular trough, there is hardly any droop due to shear.

(8) We now turn to our last illustration, that of the "gutter pipe" with the lowest point of the external surface and the highest points of the internal surface fixed as far as is feasible. The complete fixing of these points is not within the reach of the mathematical solution. We shall realise the solution by supposing the three points represented by pins parallel to the generators of the tube or portion of a tube, each carrying a nut. A rigid vertical plate has now cut in it a vertical and a horizontal slot. The two pins of the internal boundary work in the horizontal, the pin of the external surface in the vertical slot. In other words, the point on the mid-line of the external surface must have vertical play, and the extreme points on the internal surface need horizontal play. The mathematical conditions are accordingly

$$w = v = 0, \quad \text{when } r = a, \quad \theta = 0.$$

$$u = w = 0, \quad \text{when } r = a_0, \quad \theta = \pm \frac{1}{2} \gamma.$$

These conditions lead to

$$0 = \frac{W a^3}{EI} \left\{ \frac{1}{2} \eta \left( \rho \cos \frac{1}{2} \gamma - \frac{\sin \frac{1}{2} \gamma}{\gamma} \frac{1 + \rho + \rho^2}{1 + \rho} \right) - \rho^2 \sin^2 \frac{1}{2} \gamma \right\} + a,$$

which determines  $a$ . Further:

$$0 = \chi(a_0, \pm \frac{1}{2} \gamma) - \frac{W a^3}{EI} \left( \rho \cos \frac{1}{2} \gamma - \frac{\sin \frac{1}{2} \gamma}{\gamma} \frac{1 + \rho + \rho^2}{1 + \rho} \right) \rho^2 \sin^2 \frac{1}{2} \gamma \\ - \beta'' a_0 \cos \frac{1}{2} \gamma + \gamma'',$$

$$0 = \chi(a, 0) - \beta'' a + \gamma'',$$

which last two equations suffice to determine  $\gamma''$  and  $\beta$ , the first of the two

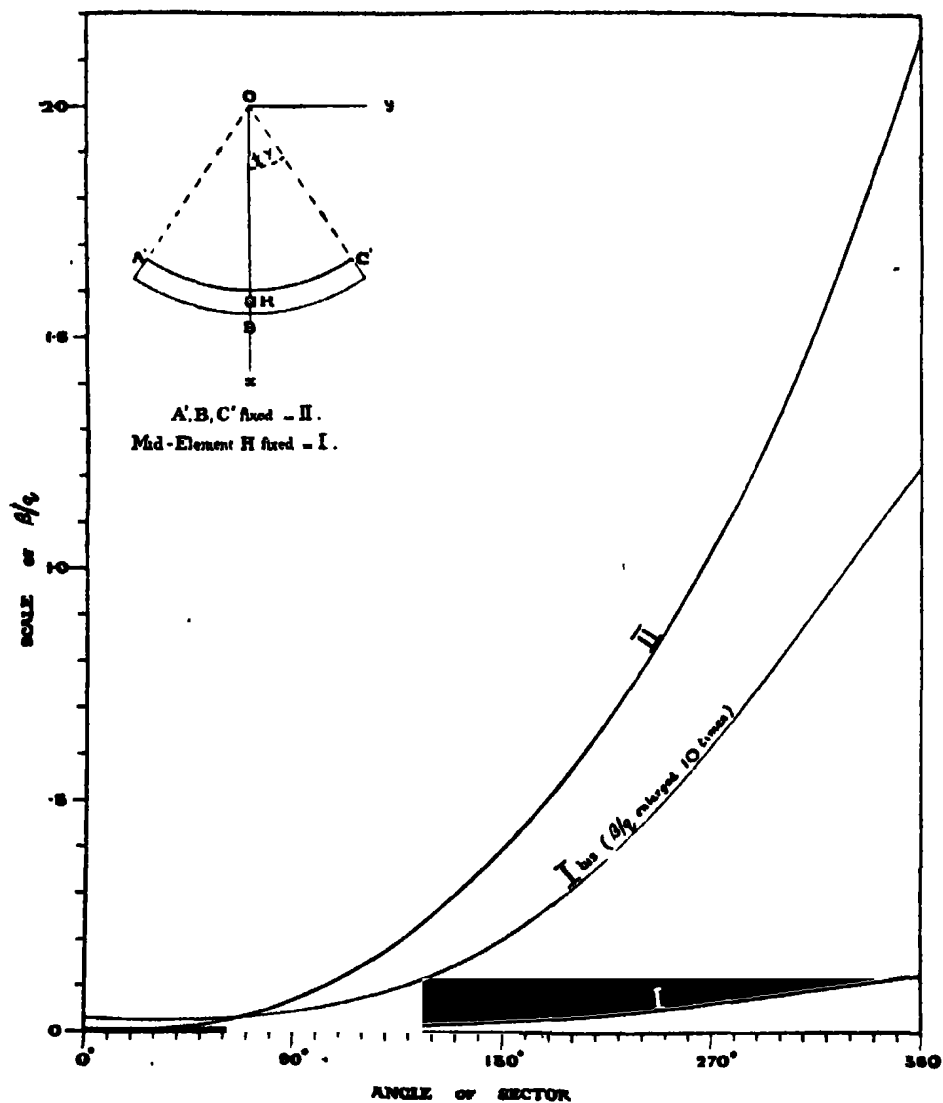


DIAGRAM II.—Curtate sectors. Fixing of a central element in de Saint-Venant's fashion (I) and fixing of lowest and two highest points (II).

being the same for either  $\pm \frac{1}{2}\gamma$ . Subtracting to get of  $\gamma''$ , we find, after considerable reductions, that

$$\begin{aligned} \beta/\gamma = & \frac{1}{2}\eta \left( \frac{4}{3} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{1+\rho+\rho^2}{1+\rho} \right)^2 + \frac{2}{3} \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{1-\rho^3}{1-\rho \cos \frac{1}{2}\gamma} - \frac{1}{4} \frac{1-\rho^3 \cos \frac{1}{2}\gamma}{1-\rho \cos \frac{1}{2}\gamma} \\ & + \frac{1}{12} (1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \frac{1-\rho^3 \cos \frac{3}{2}\gamma}{1-\rho \cos \frac{1}{2}\gamma} \\ & + \frac{1}{3} (1+\eta) \frac{\sin \frac{1}{2}\gamma}{\gamma} \frac{\rho^2}{(1+\rho)(1-\rho \cos \frac{1}{2}\gamma)} \log_e \rho \\ & - \frac{\sin \frac{1}{2}\gamma}{\gamma(1-\rho \cos \frac{1}{2}\gamma)} \left[ \sum_{i=1,3,5,\dots}^{\infty} (1-\rho^3) \frac{1+\rho^m}{1-\rho^m} \left\{ \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right\} \right. \\ & \left. - \sum_{i=2,4,6,\dots}^{\infty} (1+\rho^3) \frac{1-\rho^m}{1+\rho^m} \left\{ \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right\} \right], \quad (\text{xxxviii}) \end{aligned}$$

where  $m = 2i\pi/\gamma$ .

The infinities occur as in previous cases when  $\gamma = 2\pi$ ,  $\frac{2}{3}\pi$ , or  $\frac{1}{3}\pi$ . Since  $1-\rho \cos \frac{1}{2}\gamma$  is always positive and greater than zero, this provides no infinity.

(a.)  $\gamma = 2\pi$ . All the terms of the series vanish, owing to the factor  $\sin \frac{1}{2}\gamma$ , except the first and the third.

$$\begin{aligned} \text{Limit}_{i \rightarrow 1} \left[ \frac{-\sin \frac{1}{2}\gamma}{\gamma(1-\rho \cos \frac{1}{2}\gamma)} (1-\rho^3) \frac{(1+\rho^m)}{(1-\rho^m)} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right], \\ = \frac{1}{4} (3+2\eta) (1+\rho+\rho^2), \\ \text{Limit}_{i \rightarrow 3} \left[ \frac{-\sin \frac{1}{2}\gamma}{\gamma(1-\rho \cos \frac{1}{2}\gamma)} (1-\rho^3) \frac{1+\rho^m}{1-\rho^m} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right] \\ = -\frac{1}{8} (1-2\eta) (1-\rho-\rho^2). \end{aligned}$$

$$\text{Hence} \quad \beta/\gamma = \frac{1}{4} (3+2\eta) (1+\rho+\rho^2) - \frac{1}{4} (1-\rho+\rho^2). \quad (\text{xxxix})$$

(b.)  $\gamma = \frac{2}{3}\pi$ . The first or  $i = 1$  term becomes infinite, and we must proceed to the limit of this term in conjunction with the term in  $1/\sin \frac{3}{2}\gamma$ .

We have:

$$\begin{aligned} \text{Limit}_{i \rightarrow 1} \left[ \frac{1}{12} (1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \frac{1-\rho^3 \cos \frac{3}{2}\gamma}{1-\rho \cos \frac{1}{2}\gamma} \right. \\ \left. - \frac{\sin \frac{1}{2}\gamma}{\gamma(1-\rho \cos \frac{1}{2}\gamma)} (1-\rho^3) \frac{1+\rho^m}{1-\rho^m} \frac{24-8\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right] \\ = \frac{1+\rho^3}{1-\frac{1}{2}\rho} \frac{\sin \frac{1}{2}\pi}{\pi} \left[ \frac{1}{48} (15-6\eta) - \frac{1}{2} (1-2\eta) \frac{\rho^3 \log_e \rho}{1-\rho^6} \right]. \end{aligned}$$

Hence :

$$\begin{aligned}\beta/q &= 2\eta \left( \frac{\sin \frac{1}{2}\pi}{\pi} \frac{(1+\rho+\rho^2)^2}{1+\rho} \right) - \frac{1}{4} \frac{1-\frac{1}{2}\rho^3}{1-\frac{1}{2}\rho} \\ &\quad + \frac{\sin \frac{1}{2}\pi}{\pi} \left( \frac{1-\rho^3}{1-\frac{1}{2}\rho} + \frac{1}{16}(5-2\eta) \frac{1+\rho^3}{1-\frac{1}{2}\rho} \right) \\ &\quad + \frac{\sin \frac{1}{2}\pi}{\pi} \frac{\log_e \rho}{1-\frac{1}{2}\rho} \left( 2(1+\eta) \frac{\rho^2}{1+\rho} - \frac{1}{2}(1-2\eta) \frac{\rho^3}{1-\rho^3} \right) \\ &\quad - \frac{1}{4} \frac{\sin \frac{1}{2}\pi}{\pi} \frac{1}{1-\frac{1}{2}\rho} \left[ \sum_{i=3,5,7,\dots}^{\infty} (1-\rho^3) \frac{1+\rho^{3i}}{1-\rho^{3i}} \cdot \frac{1-\eta(3i^2-1)}{i(i^2-1)(9i^2-1)} \right. \\ &\quad \left. - \sum_{i=2,4,6,\dots}^{\infty} (1+\rho^3) \frac{1-\rho^{3i}}{1+\rho^{3i}} \cdot \frac{1-\eta(3i^2-1)}{i(i^2-1)(9i^2-1)} \right].\end{aligned}\quad (xl)$$

(c.)  $\gamma = 4\pi/3$ . The second or  $i = 2$  term becomes infinite in (xxxviii), but is balanced by the infinity of the fourth term. We find :

$$\begin{aligned}\text{Limit}_{\rho \rightarrow 2} \left[ \frac{1}{4}(1-2\eta) \frac{\sin \frac{1}{2}\gamma}{\sin \frac{3}{2}\gamma} \frac{1-\rho^3 \cos \frac{3}{2}\gamma}{1-\rho \cos \frac{1}{2}\gamma} \right. \\ \left. + \frac{\sin \frac{1}{2}\gamma}{\gamma(1-\rho \cos \frac{1}{2}\gamma)} (1+\rho^3) \frac{1-\rho^m}{1+\rho^m} \frac{24-\eta(m^2-3)}{m(m^2-1)(m^2-9)} \right] \\ = -\frac{1-\rho^3}{1+\frac{1}{2}\rho} \frac{\sin \frac{3}{2}\pi}{2\pi} \left[ \frac{15-6\eta}{48} + \frac{1}{2}(1-2\eta) \frac{\rho^3 \log_e \rho}{1-\rho^6} \right].\end{aligned}$$

Hence :

$$\begin{aligned}\beta/q &= 2\eta \left( \frac{\sin \frac{2}{3}\pi}{2\pi} \frac{1+\rho+\rho^2}{1+\rho} \right)^2 - \frac{1}{4} \frac{1+\frac{1}{2}\rho^3}{1+\frac{1}{2}\rho} \\ &\quad + \frac{\sin \frac{2}{3}\pi}{2\pi} \left( \frac{1-\rho^3}{1+\frac{1}{2}\rho} - \frac{1}{16}(5-2\eta) \frac{1-\rho^3}{1+\frac{1}{2}\rho} \right) \\ &\quad + \frac{\sin \frac{2}{3}\pi}{2\pi} \frac{\log_e \rho}{1+\frac{1}{2}\rho} \left( 2(1+\eta) \frac{\rho^2}{1+\rho} - \frac{1}{2}(1-2\eta) \frac{\rho^3}{1+\rho^3} \right) \\ &\quad - \frac{1}{4} \frac{\sin \frac{2}{3}\pi}{2\pi} \frac{1}{1+\frac{1}{2}\rho} \left[ \sum_{i=1,3,5,\dots}^{\infty} (1-\rho^3) \frac{1+\rho^{3i}}{1-\rho^{3i}} \frac{4-\eta(3i^2-4)}{i(i^2-4)(9i^2-4)} \right. \\ &\quad \left. - \sum_{i=2,4,6,\dots}^{\infty} (1+\rho^3) \frac{1-\rho^{3i}}{1+\rho^{3i}} \frac{4-\eta(3i^2-4)}{i(i^2-4)(9i^2-4)} \right].\end{aligned}\quad (xli)$$

From formula (xxxviii) to (xli) the following Table for  $\beta/q$  has been computed. It indicates straight off that the fixing of points off the axis of symmetry of the cross-section is far less effective than fixing points on the axis of symmetry in reducing the droop due to shear. The values of  $\beta/q$  are plotted as II in Diagram II :—



$\gamma$ .	$\beta q$ .	$\beta/q$ for $\eta = 0.25$ .
0	$0.001665 + 0.002082 \eta$	0.0022
12	$0.001666 + 0.000933 \eta$	0.0019
30	$0.003807 - 0.005679 \eta$	0.0024
45	$0.010922 - 0.012605 \eta$	0.0078
60	$0.024593 - 0.017785 \eta$	0.0201
90	$0.072108 - 0.018782 \eta$	0.0674
120	$0.145750 - 0.028483 \eta$	0.1386
135	$0.186386 + 0.009818 \eta$	0.1888
180	$0.369036 + 0.091291 \eta$	0.3909
225	$0.006700 + 0.247616 \eta$	0.6686
240	$0.701470 + 0.320060 \eta$	0.7816
270	$0.915986 + 0.499232 \eta$	1.0408
315	$1.208780 + 0.868110 \eta$	1.5242
360	$1.805000 + 1.355000 \eta$	2.1438

The droop due to shear is clearly of no importance until the sectorial angle reaches  $90^\circ$ . Then it rapidly increases, until  $\beta/q$  becomes about 18 times as large as for the element-fixing when we deal with a split tube.

While in the case of the complete sector we have seen that there is no substantial difference in the shearing droop between the cases of fixing a centroidal element (de Saint-Venant's method) and fixing two points on the mid-section, we see that very considerable differences arise in the case of the annular or trough section according as we fix an element on the mid-plane, or a point on the bottom and two at the top edges. The physical reasons for this great difference in shearing droop are not immediately obvious. Experimental testing of these two methods of fixing would be fairly easy, and at the same time interesting results might be obtained by fixing on the terminal a larger number of points than are compatible with de Saint-Venant's mathematical solution.

The ideal mathematical solution ought to admit any shearing stress over the free end of the cantilever, no stress over the generators of the prism, and any shifts (including the system  $u = v = w = 0$ ) over the whole of the fixed end. But, so far, such very general conditions have defied mathematical treatment. Indeed, as far as we are aware, no solution of any importance has yet been obtained for an elastic body when it is subject to given shifts over one portion and given stresses over the remainder of its surface.

*On the Relation between Wind and Distribution of Pressure.*

By HAROLD JEFFREYS, M.A., D.Sc.

(Communicated by Sir Napier Shaw, F.R.S. Received June 3, 1919.)

In studying the relation between the observed wind at various heights, and the pressure distribution at the surface of the earth, one usually takes as the standard of comparison the "geostrophic" wind, which is determined by the pressure distribution alone. If its velocity be denoted by  $G$ ,  $G$  is defined by the equation

$$2\Omega \sin \lambda \cdot \rho G = \frac{\partial p}{\partial \nu},$$

where  $\Omega$  is the earth's angular velocity of rotation,

$\lambda$  is the latitude,

$\rho$  is the density of the air,

$p$  is the pressure, and

$\partial p / \partial \nu$  is the rate of increase of pressure per unit distance normal to the isobars. Self-consistent units are of course to be employed.

The direction of this ideal wind is along the isobars, so that the low pressure is on its left.

If certain conditions were satisfied in the atmosphere, it is easily shown\* that the actual wind would always be strictly equal to the geostrophic wind (apart from conceivable free vibrations compatible with constant pressure). These conditions are that (1) the pressure distribution should not be changing with the time; (2) friction should be absent; (3) the velocity should be so small that its square can be neglected. None of these conditions holds in practice. The failure of the first is the chief reason for official encouragement of meteorology. Sir Napier Shaw has shown† that the instantaneous centre of the motion in a cyclone moving from west to east would be expected to be north of the centre of the isobars, causing the wind in front of the cyclone to blow outwards from the region of low pressure, while that on the following side blows inwards. The second disturbing influence—friction—is ordinarily the most important near the surface, but dies out at a height of a few thousand feet. Its amount depends on several factors, but chiefly on the temperature lapse rate and the wind velocity; and G. I. Taylor has shown that it causes the surface wind to deviate towards the region of

\* See, for instance, 'Phil. Mag.,' vol. 37, pp. 1-3 (1919).

† 'Geophysical Memoirs of the Meteorological Office,' No. 12, p. 35.

low pressure, while its velocity is decidedly less than that of the geostrophic wind. The third condition is usually approximately satisfied, except near the centres of cyclonic storms. If the pressure distribution were stationary, the terms neglected would amount simply to the "cyclostrophic" term of the ordinary theory; but, owing to its variation with time, they become more complex.

The observed wind at the surface has usually between 30 per cent. and 80 per cent. of the geostrophic velocity, and it generally deviates by 1 to 5 points from the isobar towards the region of low pressure. Now, the first and third of the above-mentioned disturbing influences would make the wind deviate clockwise and counter-clockwise equally often, since they produce opposite effects on two sides of a depression. The deviation in direction is therefore to be attributed mostly to friction. The same applies to the reduction of velocity. Accordingly, friction is to be regarded as the dominant cause of the difference between the actual and theoretical winds. The present investigation was undertaken to find out how much of the large range of variation in the difference, which occurred even with constant geostrophic velocity, was due to variations in the friction itself, and how much to the other neglected factors.

If  $S$  denote the velocity of the surface wind, and  $\alpha$  its deviation from the geostrophic wind, measured counter-clockwise, and if  $V$  denote  $G(\cos \alpha - \sin \alpha)$ , then Taylor showed that, provided the turbulence was the same at all heights and the system was steady,  $S$  would be equal to  $V$ . This result is independent of the amount of turbulence, so long as it does not change with height, and of the geostrophic velocity itself. This fact provided the basis for the first attack on the problem. The correlation coefficients,  $r_{SG}$  between  $S$  and  $G$ , and  $r_{SV}$  between  $S$  and  $V$ , were calculated from a series of 142 observations taken on merchant ships in the North Sea, supplied by the Marine Division of the Meteorological Office, the geostrophic wind being found from the working charts (5 mb. interval; scale 1:10000000). Only those observations for which good determinations of the gradient were available were employed. Now  $S/V$  would on the assumption to be tested always be unity, except for the effects of the variation with time in the pressure distribution and accidental errors in the determination of  $S$ ,  $G$ , and  $\alpha$ . Hence  $r_{SV}$  should be 1.00 apart from these effects.  $S/G$ , on the other hand, would depend on the variations in the pressure distribution, the turbulence, and also on  $G$  itself, as well as on the accidental errors of  $S$  and  $G$ . Thus  $r_{SV}$  would be expected to be considerably greater than  $r_{SG}$ ; for the contrary to hold would imply either that there were great accidental errors in  $\alpha$ , or that the assumption that the turbulence is independent of the

height is seriously in error. Actually, the following results were found; the winds have been classified according to the quadrant in which the geostrophic wind lies. All velocities are in metres per second.

Quadrant.	Number of Observations.	$r_{SV}$ .	$r_{SG}$ .	Mean S.	Mean G.	Mean V.	Mean $\alpha$ .
NE	15	0.66	0.51	8.3	13.1	11.7	7
SE	31	0.51	0.83	8.2	14.7	10.4	12
SW	56	0.50	0.75	7.7	15.9	12.5	16
NW	40	0.24	0.53	8.6	14.2	11.4	8

Thus, in three of the four quadrants,  $r_{SG}$  is greater than  $r_{SV}$ , contrary to what might have been expected; while the remaining one is based on too few observations to be relied upon. In no case does  $r_{SV}$  approach unity.

This result might be attributed to accidental errors in  $\alpha$ . For so low a correlation coefficient to be due to this would, however, require the standard error of  $\alpha$  to be greater than the ratio of the standard deviation of S to the mean value of S, and the range of wind velocity was such that this was of order 1. Thus  $\alpha$  would have to be liable to errors of several points. Now, the error of  $\alpha$  is the algebraic difference between those in the directions of the true and geostrophic winds. The former class are probably small; sailors' estimates of the direction are said to be very concordant and trustworthy, even in spite of the complication arising from the motion of the ship. Estimates of the direction of the geostrophic wind are open to more suspicion. The isobars on the charts are obtained by drawing smooth curves that will fit a comparatively small number of observations, and the error is therefore the sum of the error of this interpolation and that introduced in measuring the charts. As the days were selected so as to give good determinations of the gradient, the latter error was unlikely to exceed a point, but the former is, from the nature of the case, unknown. It is quite possible that the true isobars are really wavy in form, the wavelength being of the order of 100 km., and that the practice of smoothing these waves out leads to considerable errors. The smallness of  $r_{SV}$  may then be attributed to two main causes: first, great variations in turbulence with height; and second, irregularities in the isobars. The fact that S is systematically less than V might be held to support the former view, for contortion of the isobars would presumably increase and decrease S equally often; but, as a systematic under-estimation of the surface wind by the observer would act similarly, one cannot place much reliance on this.

The vertical distribution of turbulence is closely connected with the

temperature lapse-rate, and this in its turn presumably with the difference in temperature between air and sea, which is given in the ships' logs. An attempt was made to test the turbulence hypothesis on this basis, but it proved a failure, for the temperature differences recorded were less than could be accounted for by the unsatisfactory conditions of exposure in a ship, and accordingly no significance could be attached to the small correlation found.

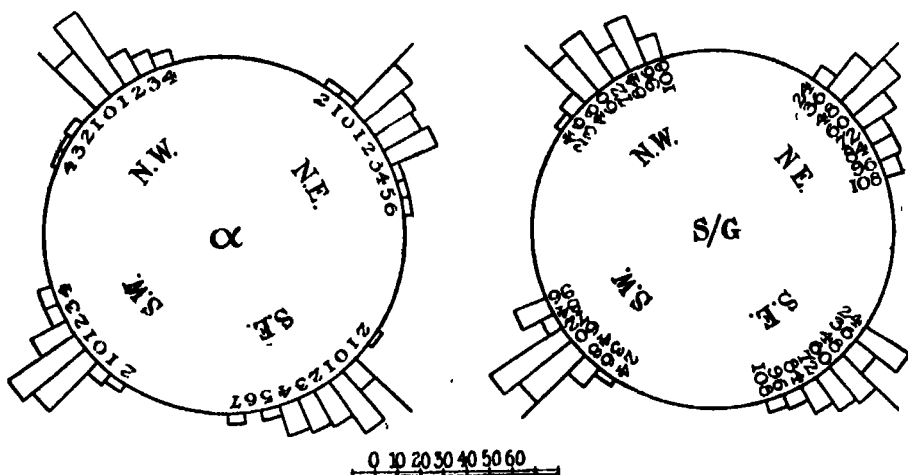
A longer series of observations, taken on ships of H.M. Navy, and kindly supplied for this purpose by the Hydrographer, was made use of in a further investigation of this question. Enough data were available for it to be possible to divide them into 16 classes, whose average number was about 40, according to the strength of the geostrophic wind and the quadrant whence it blew. Thus Tables showing the frequencies of different values of  $\alpha$  and S/G in the separate classes could be constructed; and if quadrants differed systematically among themselves, or if strong winds systematically gave larger or smaller values of  $\alpha$  or S/G than light winds, one would expect these facts to be discovered by this method. Two separate classifications were carried out: one gave in each class the number of times the surface wind veered or backed by any number of points from the geostrophic wind and the other the number of times S/G lay between any two multiples of 12 per cent. The results are given in the two following Tables (p. 239). The number in each compartment is the number of times a geostrophic wind of the appropriate class, indicated in the first column, was found to be associated with a direction deviation or velocity ratio within the limits indicated at the top. The column R includes those few instances where  $\alpha$  or S/G lay outside the limits of the Table.

These frequency distributions are shown in diagrammatic form in the figures on pp. 237, 238. In these the length of any projection from a circle is proportional to the percentage of the winds of the appropriate class that have the value of  $\alpha$  or S/G indicated by the number just inside the circle;  $\alpha$  is expressed in points, numbers on the clockwise side of the zero denoting veer of the geostrophic wind from the surface wind, while numbers on the counter-clockwise side denote backs; S/G is expressed in percentages, and all instances where it lay between consecutive multiples of 12 per cent. are grouped together.

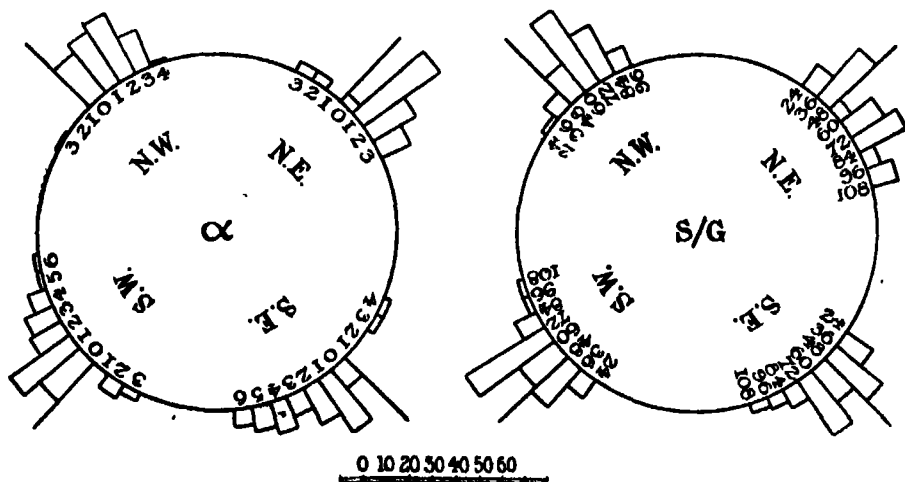
With regard to the differences in direction we notice (1) veers of over 4 points and backs of any amount are very rare. (2) there is a sudden rise in frequency between  $-1$  and  $1$  point; the decline for greater values of  $\alpha$  is much more gradual, so that the frequency curves are violently asymmetrical. In every class where it is possible to identify the commonest

deviation with any certainty the number of deviations greater than this is greater than the number of smaller deviations. Thus the asymmetry is a general property of the classes, and not a peculiarity of any particular group of wind-strengths or directions.

**LIGHT BREEZES:  $G$  under  $8.5 \text{ m/s}$**



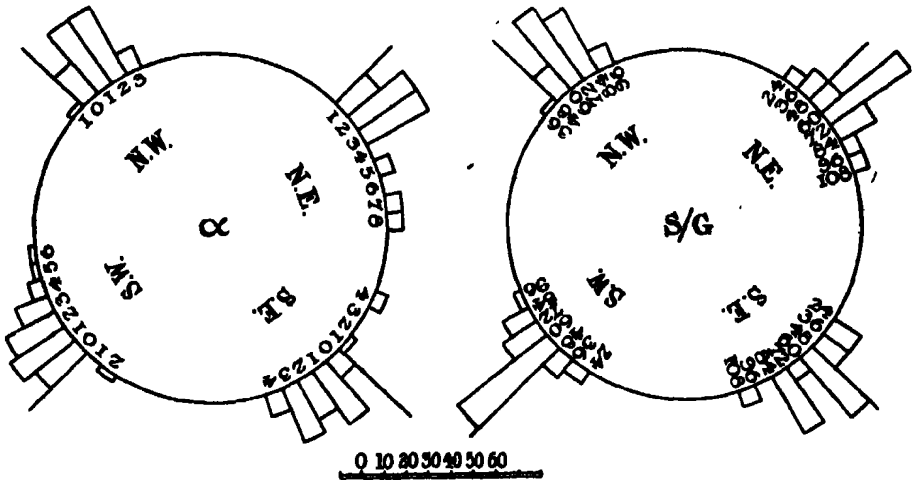
**STRONG BREEZES:  $G$  8.5 to  $12 \text{ m/s}$**



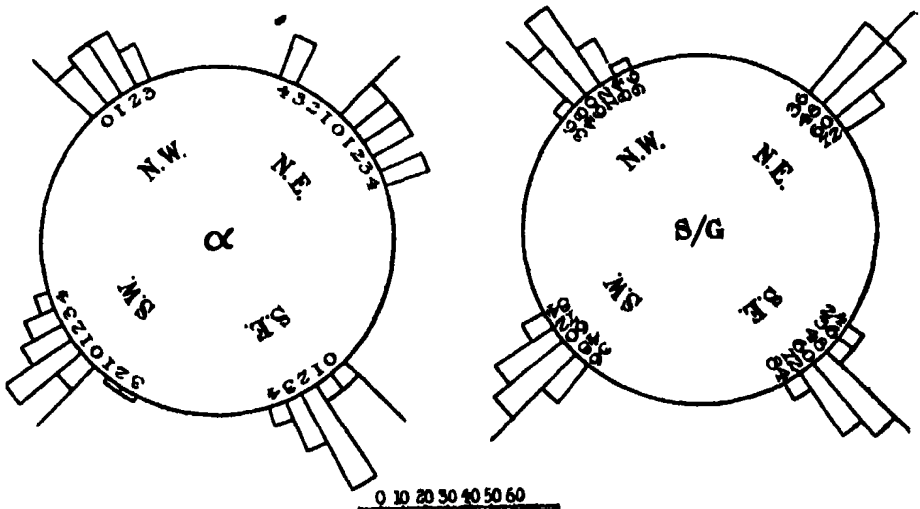
This asymmetry provides a further argument against the attribution of unexplained variations in  $\alpha$  to observational error. For the directions of the geostrophic and true winds are both directly observed, and there is no reason in either case why errors of opposite signs should be unequally probable. Thus the deviation-frequency curves, if observational error played a large

part in their determination, should be symmetrical; or if the number of observations per class were insufficient to give symmetrical curves, the mode

**STRONG WINDS: G 12.5 to 18 m/s**



**GALES: G over 18.5 m/s**



would not lie systematically oftener on one side of the mean than the other. We must, therefore, look elsewhere for the cause of the skewness.

Table I.—Deviation of the Surface Wind from the Gradient.

Deviations (in points).	-6.	-5.	-4.	-3.	-2.	-1.	0.	1.	2.	3.	4.	5.	6.	7.	E.	Totals.
<b>Quadrant</b>																
0 to 8	0	0	0	0	1	1	9	7	5	7	1	1	6	0	0	33
8.5 12	0	0	0	1	1	0	1	9	5	3	0	0	0	0	1	20
N.E. 12.5 18	0	0	0	0	0	0	3	5	5	0	1	0	1	1	1	17
over 18	0	0	1	0	0	0	1	1	1	0	1	0	0	0	0	5
0 to 8	0	0	0	0	1	0	5	12	9	7	6	2	0	2	1	44
8.5 12	0	0	1	1	0	0	5	12	8	4	7	5	3	0	1	47
S.E. 12.5 18	0	0	2	0	0	1	3	9	0	8	3	0	0	0	0	32
over 18	0	0	0	0	0	0	1	1	6	3	1	0	0	0	0	12
0 to 8	0	0	0	0	1	2	11	13	6	2	2	0	0	0	0	37
8.5 12	0	0	0	1	2	0	11	15	7	6	4	1	1	0	0	48
S.W. 12.5 18	0	0	0	0	1	0	16	21	17	11	5	0	1	0	0	72
over 18	0	0	0	1	1	0	5	12	7	5	2	0	0	0	0	33
0 to 8	0	0	1	1	2	0	13	21	7	5	3	0	0	0	1	54
8.5 12	0	0	0	1	0	0	11	13	15	9	1	0	0	0	0	50
N.W. 12.5 18	0	0	0	0	0	1	7	14	14	4	0	0	0	0	0	40
over 18	0	0	0	0	0	0	5	6	6	4	0	0	0	0	0	21
<b>Total</b> ....	0	0	5	6	10	5	107	171	123	78	38	9	7	3	5	566

Table II.—Frequencies of different Values of S/G.

S/G as per cent.	24-36.	36-49.	49-60.	60-72.	72-84.	84-96.	96-108.	E.	Totals.
<b>Quadrant</b>									
0 to 8	2	7	8	5	3	3	2	3	33
8.5 12	2	5	1	3	4	1	2	2	20
N.E. 12.5 18	1	2	2	7	3	1	1	0	17
over 18	0	2	2	1	0	0	0	0	5
0 to 8	10	5	9	8	6	3	2	1	44
8.5 12	6	12	8	13	4	2	1	1	47
S.E. 12.5 18	4	4	11	2	9	0	2	0	32
over 18	1	1	5	4	1	0	0	0	12
0 to 8	1	4	11	14	2	5	0	0	37
8.5 12	4	10	9	19	4	1	1	0	48
S.W. 12.5 18	4	7	36	12	9	2	0	2	72
over 18	0	7	13	10	3	0	0	0	33
0 to 8	1	3	11	13	7	12	7	0	54
8.5 12	1	4	8	19	12	5	0	1	50
N.W. 12.5 18	0	1	6	16	13	4	0	0	40
over 18	0	1	6	9	4	1	0	0	21
<b>Totals</b> .....	37	74	146	155	84	40	18	10	566



The error introduced in smoothing the isobars may perhaps be a cause, but there are difficulties in the way of supposing it to be the chief. Suppose for the sake of definiteness that the smoothed isobars are straight and parallel, and that the corresponding geostrophic wind is south-west. Then the above counts show that the surface wind is likely to be anything from south-west to south, and it is more likely to be one of south-west and south-west by south than to be one of south-south-west, south by west, or south. If the true isobars were sine curves, and the deviation caused by turbulence constant, the deviation-frequency curve would be symmetrical; for the sine curves would give a frequency distribution symmetrical about  $\alpha = 0$ , and the constant effect of turbulence would merely amount to shifting this curve bodily to one side. Suppose, however, that the turbulence gives a constant deviation and that the true isobars systematically cross the smoothed ones from west to east at a smaller angle than from east to west. Then throughout the long stretches where the mutual inclination is small the effect of turbulence is partly counteracted by the slope, while they combine in the short stretches where the slope is great and reversed. Thus most of the deviations would be small; there would be few great ones, and the frequency curve would be notably asymmetrical in just the observed way.

So far this suggestion, therefore, appears satisfactory; but its fundamental hypothesis is difficult to grant. Why should the true isobars *systematically* cross the smoothed ones at a smaller angle one way than the other? Why should this occurrence be practically independent of the direction of the isobars themselves? Until we have direct theoretical or observational reason to believe in this peculiar systematic contortion of the true isobars, we should prefer a hypothesis that does not require it. There remains yet another difficulty. If the normal distance between consecutive smoothed isobars be  $h$ , and if  $\alpha_0$  be the deviation caused by turbulence and  $\alpha_1$  the inclination of the true isobar to the smoothed one, we have

$$\alpha = \alpha_0 + \alpha_1.$$

Also the normal distance between consecutive true isobars is reduced to  $h \cos \alpha_1$ , so that the true geostrophic wind is proportional to  $\sec \alpha_1$ . Hence, since  $G$ , the geostrophic wind derived from the smoothed isobars, varies only slowly, the value of  $S/G$  obtained should show an intimate relation with  $\sec \alpha_1$ , i.e., with  $\sec(\alpha - \alpha_0)$  where  $\alpha_0$  is a constant. The theory leaves little room for inaccuracy in this; but it will be seen later that the correlation between  $S/G$  and  $\alpha$  is so slight that it is even possible to doubt its sign. This fact amounts practically to disproof of the hypothesis that the asymmetry is due to contortions in the true isobars; such contortions probably give only

a fairly symmetrical variation in  $\alpha$  which is largely masked by the asymmetrical variation due to some other cause.

Changes in the distribution of pressure cause the velocity and direction to differ somewhat from the values they would have if the distribution were steady. If, however, such changes could give rise to an asymmetrical frequency distribution, the asymmetry in a cyclonic disturbance would presumably be different in front from behind. Suppose, for instance, that this caused a frequency distribution in the south-west quadrant in which the commonest deviation was  $A$ , and more winds deviated by more than  $A$  than by less than  $A$ . Then if the commonest deviation in the north-east quadrant were  $B$ , we should expect that more winds there would deviate by less than  $B$  than by more. A similar reversal would hold between the north-west and south-east quadrants. Actually we find that though the asymmetry is not equally pronounced in all quadrants, it nevertheless acts in the same direction in all. Thus the most important cause to consider is one that will always make more winds deviate by more than the mode than deviate by less. Causes acting sometimes one way and sometimes the other may be fairly important; but it is clear that they cannot be the most important, for then the frequency distribution would sometimes have its asymmetry reversed in an indubitable manner, which never occurs. Thus the motion of the isobars is not the most important cause, whether it operates through the inertial terms in the equations of motion or through the difference in time between the wind and pressure observations.

The disturbing cause not yet considered and rejected is turbulence. This term is here used in its widest possible sense. Atmospheric eddies are of many kinds, being produced by any agency that can cause local instability. The friction of the wind over a flat surface, for instance, causes small eddies to form near it, and these rise through the air, spreading out and becoming less violent as they go (like ordinary smoke rings) and taking with them their momentum and heat. Wind blowing past an obstacle would in the ideal cases considered in hydrodynamical theory give a definite surface with different velocities on its inside and outside; actually this is only an approximation, for this state is unstable, eddies form along the surface, and their motion causes a transfer of momentum which reduces the discontinuity. Air heated uniformly all over the bottom gradually acquires a temperature lapse-rate greater than the adiabatic; when this happens the system becomes unstable, and convection currents are formed. Lord Rayleigh has shown\* that the diameters of the regions of rising air will be comparable with, but probably greater than, the height of the homogeneous atmosphere: thus they are on a

\* 'Phil. Mag.,' vol. 32, pp. 529-546 (1916).

Table III.—Frequency of Association of Large or Small Values of  $\alpha$  with Large or Small Values of  $S/G$ , distributively.G is measured in metres per second ;  $\alpha$  is measured in points.

## A. Geostrophic Wind in the N.E. Quadrant.

G.	0 to 8.		8.5 to 12.		12.5 to 18.		Over 18.
$\alpha$ .	-6 to 1.5		-6 to 1.5.		-6 to 1.5.		-6 to 1.5.
$S/G$ 0 to 0.54 0.54 1.08	6 10	5 8	$S/G$ 0 to 0.54 0.54 1.08	6 8	$S/G$ 0 to 0.54 0.54 1.08	3 6	$S/G$ 0 to 0.54 0.54 1.08
Sign of combination-coefficient	Doubtful		Doubtful		Doubtful		Doubtful.

## B. Geostrophic Wind in the S.E. Quadrant.

G.		0 to 8.		8.5 to 12.		12.5 to 18.		Over 18	
a.		-6 to 1.5.		-6 to 1.5.		-6 to 1.5.		-6 to 2.5. 3 to 7.	
S/G								S/G	
0 to 0.54		5 10		7 19		10 7		0 to 0.60 4 3	
0.54 1.08		11 10		12 7		6 7		0.60 1.08 3 1	
Sign of combination-coefficient		Negative		Negative		Probably positive		Probably negative.	

Table III—(continued).  
C. Geostrophic Wind in the S.W. Quadrant.

G.	0 to 8.		8.5 to 12.		12.5 to 18.		Over 18.		
a.	-6 to 1.5.    2 to 7.		-6 to 1.5.    2 to 7.		-6 to 1.5.    2 to 7.		-6 to 1.5.    2 to 7.		
S/G 0 to 0.60 0.60 1.08	11 16	5 5	S/G 0 to 0.60 0.60 1.08	16 13	S/G 0 to 0.54 0.54 1.08	13 26	S/G 0 to 0.60 0.60 1.08	12 7	6 6
Sign of contin- gency co- efficient	} Probably negative		Positive		Negative		Doubtful.		

D. Geostrophic Wind in the N.W. Quadrant.

G.	0 to 8.		8.5 to 12.		12.5 to 18.		Over 18.	
a.	-6 to 1.5.	2 to 7.	-6 to 1.5.	2 to 7.	-6 to 1.5.	2 to 7.	-6 to 1.5.	2 to 7.
S/G 0 to 0.60 0.60 1.08	10 23	3 11	S/G 0 to 0.66 0.66 1.08	11 15	S/G 0 to 0.66 0.66 1.08	7 16	S/G 0 to 0.66 0.66 1.08	7 5
Sign of contin- gency co- efficient	Probably negative		Probably negative		Probably negative		Probably positive.	

very different scale from the ordinary frictional eddy. Yet they resemble it in providing a mode of transfer, by irregular mass-motion, of momentum and heat; they thus produce a pseudo-viscosity. Local kinds of instability, such as great temperature lapse-rates at particular heights, also give rise to eddy motion on an intermediate scale; examples are afforded by sea-fog and by most clouds.\* The combination of a great lapse-rate with a wind naturally produces eddies more readily than either of these acting alone.

Enough has been said, therefore, to indicate that the distribution of turbulence in the atmosphere depends mostly on the wind velocity and on the temperature lapse-rate. Both of these are very variable, and accordingly so is the turbulence. The effect of turbulence is proportional to a certain coefficient  $k$ , the eddy-viscosity, whose value at any point is proportional to an average of the product of the range of variation of the wind velocity there into the size of the average eddy that gets there. Near the ground the size of the eddies is small, but the velocity varies a great deal. The higher one goes, the more of the turbulence takes the form of convection; the size of the eddies becomes comparable with the height of the troposphere, while the relative velocity of their parts diminishes. As these two changes produce opposite effects on the eddy-viscosity, it is impossible to predict on these grounds whether it should increase or diminish with height. Taylor dealt with the simplest case, where the coefficient is independent of the height, and showed that if this were true we should always have

$$S/G = \cos \alpha - \sin \alpha.$$

The deviation  $\alpha$ , measured counter-clockwise from the isobar, should always be positive and less than four points ( $45^\circ$ ). It is, of course, a function of  $G$  and  $k$ . An intimate correlation should therefore be traceable between  $S/G$  and  $\alpha$ . It has already been pointed out that such a correlation would always exist, also, if the deviations were mostly due to contortion of the true isobars; thus both these hypotheses can be tested by looking for it. This was done by means of simple 4-cell contingency tables. In each class the wind observations were reclassified according to the values of  $\alpha$  and  $S/G$ . It was found that in the 16 classes the signs of the contingency coefficients occurred as follows:—

Definitely positive, 1; doubtfully positive, 2; quite uncertain, 5; doubtfully negative, 5; definitely negative, 3 (pp. 242-243).

Thus no uniformity was traceable; even where the sign of a contingency-coefficient was clear the magnitude was not great; so that altogether, while

\* G. I. Taylor, "The Formation of Fog and Mist," 'Proc. Roy. Met. Soc.,' vol. 43, pp. 241-268 (1917). Capt. C. K. M. Douglas, "The Lapse-Line and its Relation to Cloud Formation," 'Journ. Scott. Met. Soc.,' vol. 17, pp. 133-147 (1917).

there is a faint connection, large values of  $\alpha$  tending to correspond to small values of  $S/G$ , the effect is insignificant in comparison with the actual range of variation of both quantities. The principal cause of the variation is therefore one that does not lead to a strong correlation between  $S/G$  and  $\alpha$ , and both of the hypotheses that led us to expect such a correlation are therefore untenable.

We therefore conclude that the turbulence coefficient  $k$  is ordinarily a function of the height above the ground. Let us then see whether variations with height are capable of producing such irregularities as are observed. As the effects of changes in the distribution of pressure and wind with time, and second order terms in the equations of motion, have been shown to be of secondary importance in this connection, they will be neglected. Let the co-ordinates be  $x, y, z$ , where  $z$  is measured vertically upwards, and let the horizontal components of velocity be  $u$  and  $v$ . Put  $\Omega \sin \lambda = \omega$ . With the appropriate approximations the equations of horizontal motion reduce to the form

$$\begin{aligned} -2\omega\rho v &= -\frac{\partial p}{\partial x} + k\rho \frac{\partial^2 u}{\partial z^2}, \\ 2\omega\rho u &= -\frac{\partial p}{\partial y} + k\rho \frac{\partial^2 v}{\partial z^2}. \end{aligned}$$

Take the axis of  $x$  along the surface isobars, so that

$$\frac{\partial p}{\partial x} = 0.$$

If  $k$  were 0 there would be no friction, and the geostrophic condition would hold. Hence we have

$$2\omega G = -\frac{\partial p}{\partial y},$$

and therefore the equations of motion are

$$\begin{aligned} 2\omega v + k \frac{d^2 u}{dz^2} &= 0, \\ -2\omega u + k \frac{d^2 v}{dz^2} &= 2\omega G. \end{aligned}$$

Put  $u + iv = w$ . Then these equations combine into the single one

$$k \frac{d^2 w}{dz^2} - 2i\omega w = -2i\omega G.$$

So far the law of variation of  $k$  has not been specified. Suppose, for illustrative purposes, that it can be expressed in the form

$$k = k_0(1 + \lambda z)^n,$$

where  $k_0$  and  $\lambda$  are constants. Put  $1 + \lambda z = \zeta$ . Then

$$k_0 \lambda^2 \zeta^2 \frac{d^2 w}{d \zeta^2} - 2 i \omega w = -2 i \omega G.$$

The solutions of this are of the form

$$A \zeta^m + B \zeta^n + G,$$

where  $m$  and  $n$  are the rates of the equation in  $\gamma$

$$k_0 \lambda^2 \gamma (\gamma - 1) - 2 i \omega = 0,$$

and  $A$  and  $B$  are constants as yet undetermined. We have  $m + n = 1$ , and therefore the sum of their real parts is 1. Hence either  $m$  or  $n$  must have a positive real part. Let this be  $n$ . Then  $\zeta^n$  tends to infinity with  $z$ , and hence the condition that the velocity at a great height shall not tend to infinity is that  $B = 0$ . Then

$$w = G + A \zeta^n.$$

At the surface

$$w = S e^{i\alpha}.$$

Hence

$$A = S e^{i\alpha} - G.$$

The skin friction at the surface is equal in magnitude to  $\kappa \rho S^2$  per unit area, where  $\kappa$  is a constant. It acts in the direction opposite to the velocity. It must be equal to  $k\rho$  times the rate of shear in the air near the surface; hence

$$\kappa \rho S^2 e^{i\alpha} = - \int_0^\infty k \rho \frac{d^2 w}{dz^2} dz = - k_0 \rho m \frac{m-1}{m+1} A \lambda.$$

Hence  $S e^{i\alpha} - G$  has the same phase as  $-\frac{(m+1)e^{i\alpha}}{m(m-1)}$ . If the argument of  $m \frac{m-1}{m+1}$  is the constant  $\beta$ , we have by equating the ratios of real and imaginary parts on the two sides

$$\frac{G \sin \alpha}{S - G \cos \alpha} = -\tan \beta,$$

whence

$$S/G = \cos \alpha - \sin \alpha \cot \beta.$$

Put  $8\omega/k_0\lambda^2 = \tan \eta$ . Then  $\eta$  is a constant between 0 and  $\frac{1}{2}\pi$ , and

$$m = \frac{1}{2} - \frac{1}{2} \sec^2 \eta (\cos \frac{1}{2} \eta + i \sin \frac{1}{2} \eta).$$

From this we can see that  $\cot \beta$  vanishes when  $\eta = 0$ , that is, when the turbulence is infinite, and reaches unity when  $\eta = \frac{1}{2}\pi$ . The latter is Taylor's case, corresponding to  $\lambda = 0$ . Thus when the turbulence is the same at all heights

$$S = G (\cos \alpha - \sin \alpha),$$

but when  $\lambda$  is different from zero, whether positive or negative,  $S$  is greater than is given by this equation; it is never greater than  $G \cos \alpha$ .

It must be noted that when  $\lambda$  is positive, the eddy viscosity is finite on the ground and steadily increases with height; when  $\lambda$  is negative, it is finite on the ground, decreases to zero at a height  $1/\lambda$ , and then tends to infinity with the height. We may then infer that great turbulence aloft increases  $S/G (\cos \alpha - \sin \alpha)$ ; presumably if the turbulence decreases with height this ratio is reduced. Taylor found\* that the means of large numbers of observations made this ratio practically unity; this indicates that if we write  $S/G = \cos \alpha - h \sin \alpha$ , the mean value of  $h$  is about 1, though the study of individual observations here carried out shows that it must vary over a wide range. Deviations of more than four points can easily occur, for  $\alpha$  is only restricted to be less than  $\beta$ , which may reach  $90^\circ$ . Negative values of  $\alpha$  seem impossible to account for by turbulence alone. They rarely occur, and when they do are probably to be attributed to contortion of the isobars of sufficient amount to counteract the effect of turbulence. The occasional surface winds equal to or even greater than the geostrophic wind are probably due to the same cause. Such contortion is presumably frequent; for in the straight isobar regions on the map local showers are common, indicating areas of low pressure and, therefore, curvature of the isobars. Though it is not the chief factor in determining the relation of the surface wind to the gradient, as has already been shown, it may, therefore, have a very important complicating influence.

We may, therefore, conclude that the chief, but not the only, cause of the observed variations in the relation of the surface wind to the gradient is variation in the vertical distribution of turbulence. This vertical distribution is not, however, usually known, though information is gradually being accumulated from various sources.† It is presumably closely correlated with the lapse-rate of temperature; this in its turn is correlated with the time of day and plays an important part in determining the occurrence of cloud and fog. Now as a rule the wind determined by pilot balloon ascents is found to agree fairly closely with the geostrophic wind at altitudes of 3,000 feet and more; above this the change of velocity is usually small, and the value of the eddy viscosity is, therefore, immaterial, since it only enters the equations of motion through vertical variations in the velocity. The lapse-rate above this height, therefore, has little effect on the relation of the surface wind to the gradient. It may, however, be more or less correlated with the lapse-rate below this level, and in that case there should be a correlation

\* 'Phil. Trans.,' vol. 115, pp. 1-26 (1915).

† C. K. M. Douglas, *loc. cit.*



between cloud-form and the relation of the lower winds to the gradient. A year's observations at South Farnborough, provided by Mr. R. A. W. Watt, were worked up for this purpose, but no satisfactory correlations were traced. The deviations were systematically greater than at sea, presumably owing to greater surface friction; but those at 1,000 feet and above were never sufficiently greater than their standard deviations (within classes for which the cloud-form was the same) for any prediction to be possible. In the largest class, where the clouds were st. or st.cu., covering more than half the sky, the mean value of  $\alpha$  was 2.7, and its standard deviation 1.2 points; when there were no clouds below the al.cu. level the mean value of  $\alpha$  was 3 points and its standard deviation 1.0 point. Thus there was no striking correlation between cloud-form and deviation in direction.

#### *Summary.*

A classification of some 600 wind observations over the North Sea, according to their velocities and directions, showed that the most striking feature of the resulting values was their asymmetrical frequency distribution. From the fact that this was noticeable in nearly every class, it was inferred that it could be produced only by variation in turbulence or systematic contortion of the isobars on a scale too small to be recorded on the weather map. The latter cause, however, and also such variations in turbulence as keep the coefficient of eddy viscosity the same at all heights, would lead to strong correlations between  $S/G$  and  $\alpha$ , which are not observed. Hence it is concluded that the principal cause of variation in the relation of the surface wind to the gradient is variation in the vertical distribution of turbulence; and it is shown that such variation could give the effects actually observed. To complete the test of the theory it is necessary to have direct quantitative information on this distribution, which is not yet available; but the evidence already accumulated is sufficient to make it extremely probable that some information on the distribution, and hence on the lapse-rate below 3000 feet, could be obtained by prediction from the observed relation between the surface wind and the geostrophic wind.

[*Note added July 17th.*—A physical account may be given of the influence of vertical variations of turbulence. Suppose the turbulence to be confined to a very thin layer over the ground. Then above this the wind will have practically the geostrophic value, while in the layer itself the friction on the lower surface will far exceed the geostrophic terms in the equations of motion, on account of the rapidity of the shearing. Hence the motion in this will be much as if the rotation of the earth were ignored, and hence

the deviation in direction will be insignificant. The friction will nevertheless make the surface velocity less than the geostrophic velocity. In this case, therefore,  $\cos \alpha - \sin \alpha$  is nearly 1, and  $S/G$  is less than 1. Thus, if the turbulence decreases with height, we should expect to find  $S/G$  less than  $\cos \alpha - \sin \alpha$ ; it was found previously that if it increases with height  $S/G$  will be greater than  $\cos \alpha - \sin \alpha$ .]

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*On a New Method of Driving off Poisonous Gases.*

By Mrs. HERTHA AYRTON.

[PLATE 4.]

(Communicated by Prof. T. Mather, F.R.S. Received August 29, 1917.)\*

On May 6, 1915, shortly after the first German gas attack, I read a paper before this Society, dealing with the variations of pressure, and consequent currents, set up in oscillating water by an obstacle on the ground under the water. After the meeting, it occurred to me that, by oscillating an obstacle in an appropriate manner in the air close to our trenches, it ought to be possible to set up currents similar to those in the water, which, while sending the noxious gas back towards the enemy, would, at the same time, keep our men well supplied with fresh air from behind. The obstacle must be some kind of fan, and I thought smoke might represent the gas for experimental purposes.

*Smoke Apparatus.*

Smoke of the right kind was not easy to produce, the difficulty being that it had to be heavier than air, as the noxious gases were said to be. At last, however, after many trials, I found that smouldering brown paper gave very satisfactory results, if treated in the right way. It was burnt in a biscuit tin, A (fig. 1), from which the smoke rose through a tube, B, to another box, C, issuing through a second tube, D. When this whole arrangement, except the box A, was kept wrapped in wet cloths, the smoke, cooled by the evaporation of the water and by passing through the box C, became heavier than air, and fell almost like water from the mouth of the tube D on to one end of the Table E (6 feet by 3 feet), which had a barrier, F, at that end, to protect the smoke from accidental draughts. On reaching the table, the smoke

\* Held by the Society for deferred publication after the War.

expanded both in height and in width, and rolled in a very realistic manner towards the further end of the table, where a miniature parapet, G, had been

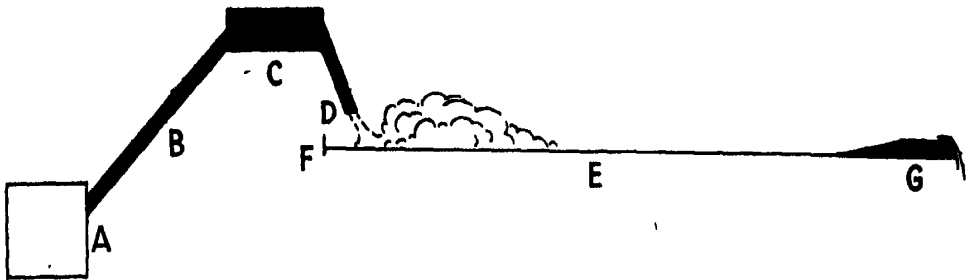


FIG. 1.—Apparatus for producing smoke heavier than air. A, Burning chamber; B, chimney; C, cooling chamber; D, outlet; E, table representing ground; F, position of draught screen; G, miniature parapet.

made, forming a dense cloud, 2 feet to 3 feet wide and some 3 inches to 4 inches high (See fig. 2, *a*, Plate 4.)

#### *Model Fan.*

My first fan was a small card on a horizontal axle, which I could alternately twirl and stop, to give the impulses to the air. This gave surprisingly good results, but not good enough. Then, remembering some startling air currents I had once observed after dropping one end of a glass tank on to a table, I thought I would try striking the parapet to give the impulses. I therefore attached a handle, at a convenient angle, to a slip of wood 4 inches by 3 inches, and with this beat with quick strokes upon the parapet G (fig. 1). The effect upon the cloud of smoke advancing from the other end of the table was miraculous (see Plate 4). After a few seconds it first stopped, and then fled backwards as if pursued, increasing in height as it went, as if it were being brushed back (*b*, fig. 2). It never stopped till it was well behind the smoke-box A (fig. 1) about 8 feet from the fan. Even the stream of smoke that continued to pour from the outlet D (fig. 1) was affected, being converted into a vibrating stream which rose and poured back over the smoke apparatus instead of falling and advancing as before (*c*, fig. 2). The smoke continued its backward course for some little time after the beating was stopped, and finally the whole table and smoke apparatus became completely cleared—an area of about 8 feet by 3 feet.

The next thing was to see if a still smaller fan would clear this same area. Fans of various sizes and shapes were tried, and modifications which were found beneficial were introduced, such, for instance, as a “back” to prevent any of the air from being expelled backwards towards the operator; and two

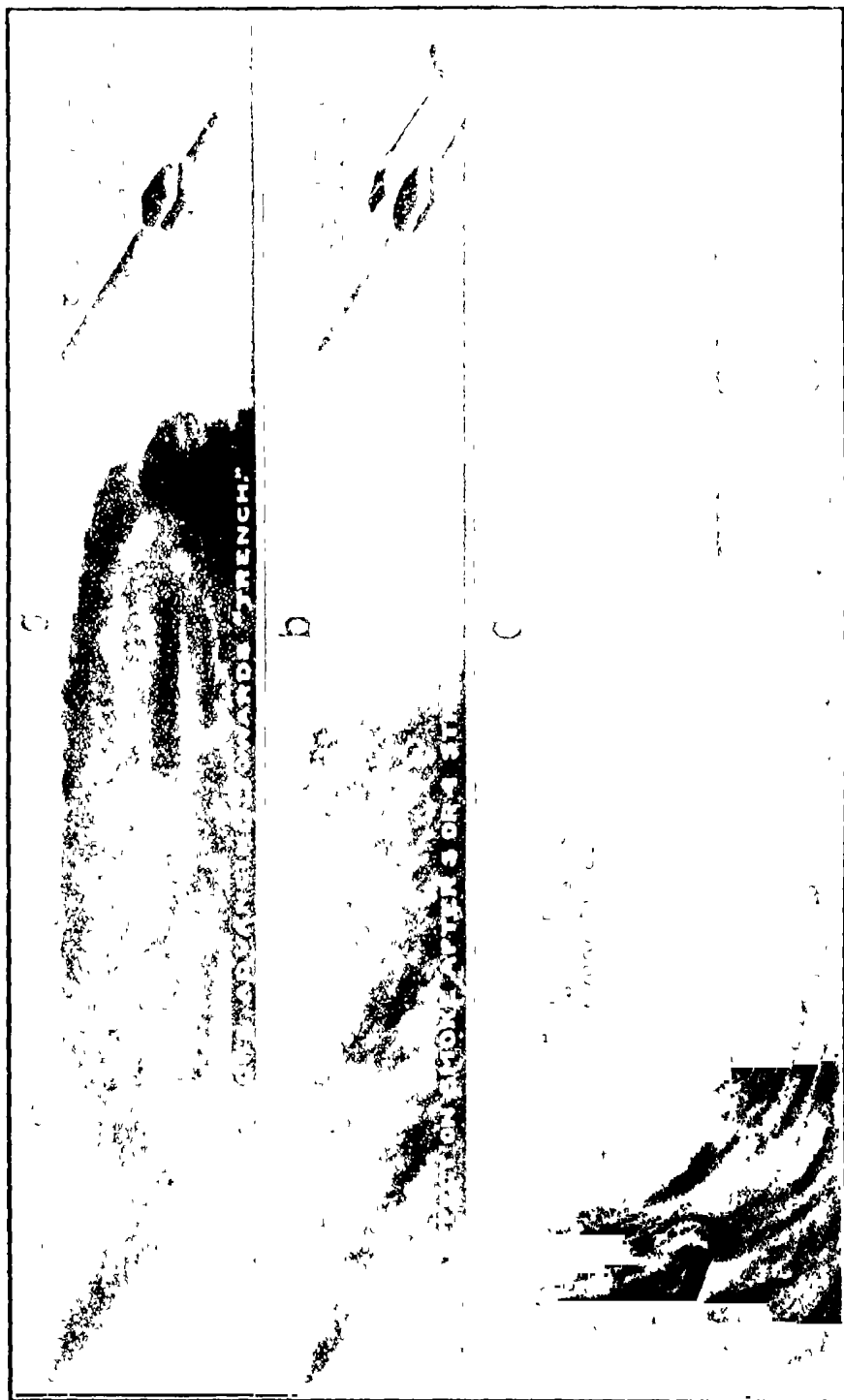


FIG. 2.—Table experiment in three stages: *a*, Smoke unchecked; *b*, smoke after three or four strokes; *c*, smoke after twelve to fifteen strokes.



hinges—one between back and blade, and the other in the blade itself—each of which allowed the parts it connected to move through a certain angle only. The final result was a fan (fig. 3) with a blade  $1\frac{1}{2}$  inches square only,

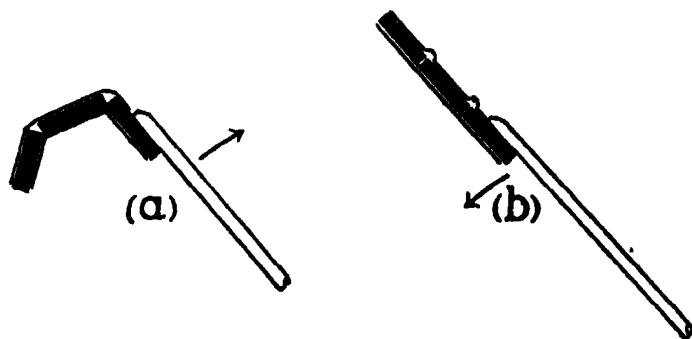


FIG. 3.—Small model fan (drawing two thirds of size of model) with which a cloud of smoke 8 feet long, 6 feet wide, and 3 inches high was cleared in 6 seconds. (a) Shows fan in upward stroke; (b) in downward stroke.

including the back. By tapping with this minute object on the parapet G (fig. 1) for about 6 seconds, at the rate of four taps a second, I cleared the table and smoke apparatus of an advancing cloud of smoke about 3 inches high; and even a width of  $1\frac{1}{2}$  feet extra on each side of a 3-foot wide table, made by extending the tablecloth, was cleared at the same time. As the height of the smoke apparatus was about  $1\frac{1}{2}$  feet, the air disturbance created by this fan with a blade of  $1\frac{1}{2}$  inches square was at least 8 feet long, 6 feet wide and  $1\frac{1}{2}$  feet high.

#### *Army Fan.*

It remained to be seen whether a fan as large as a man could easily wield would give results great enough to be of real use at the Front. The type shown in fig. 4 is the survivor of many models, made of various materials, and of different sizes and forms. It has been in daily use at the Front since May, 1916; principally for clearing trenches, dug-outs, shell holes, mine craters, etc., of the foul gases that always accumulate in them under shell fire. These can now be cleared in from a few seconds to a few minutes, and can, therefore, be consolidated immediately after taking, instead of having to be left for hours, and sometimes for days, before they can be entered.

The Army fans are made of waterproof canvas stiffened with cane, with a wooden handle. The blade has a semi-rigid centre, A, B, C, D, with loose end and side flaps; and the back has an extra very limited hinge, E, in it to enable it to accommodate itself to the varying shapes of the backs of

parapets, corners of traverses, etc. They are 3 feet 6 inches long, have a blade 15 inches square, weigh less than 1 lb. each, and can be folded and carried

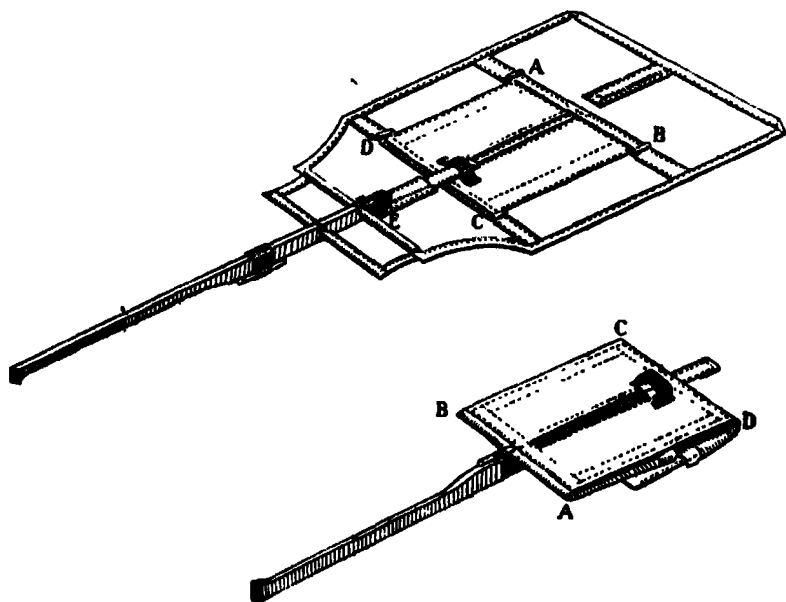


FIG. 4.—Army fan, open and folded up. (1) Opened, showing upper side; (2) as folded up. (The handle is longer than shown.)

in the braces behind the pack. These hand-worked fans are not powerful enough to repel gas-wave attacks in the comparatively high winds employed during the later phases of the war, but in the winds of from 2 to 4 miles an hour in which the earlier attacks were made, the fans could, I believe, easily have coped with them. I myself, on a practically windless day, have driven back smoke in considerable quantities in the open, 60 feet to the smoke box, and then a further 15 feet over trees from 12 feet to 15 feet high. I have now (June, 1917) devised a mechanically driven fan, however, which should be able to drive back large quantities of gas in any wind.

#### *Information Derived from Testing Fans.*

In the course of tests applied to various models, for comparing efficiencies, etc., certain facts were established that throw some light on the air problems connected with the fans. For making the tests I erected a parapet (A, fig. 5) in my laboratory, about 4 feet high and 3 feet deep, with a clear space of 33 feet in front of it and of about 3 feet behind. When a fan rested on the parapet as if in the act of striking, its tip was 35 feet from the far end of the room, where a large smoke apparatus was placed, which could pour forth a

cloud of cooled smoke 3 feet high over the whole width of the room. Behind the smoke apparatus was a double French window, either or both doors of which were left open during smoke experiments, according to the wind, so that any air current thus created drove the smoke towards the fan. It was found that five strokes of the fan on the parapet drove the smoke back, after a short pause, over the smoke box and out of the window 35 feet away.

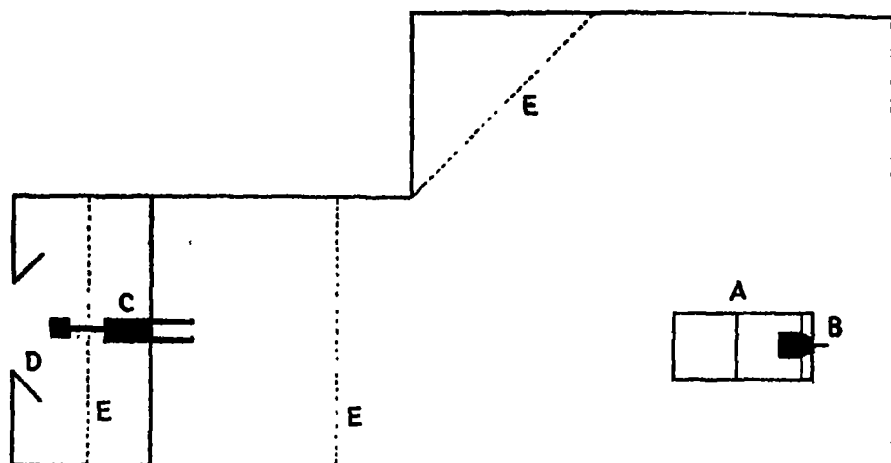


FIG. 5.—Plan of room 40 feet long, showing relative positions of parapet, fan, smoke apparatus, window, and disturbance indicators. A, Parapet; B, fan; C, smoke apparatus; D, French window; EEE, indicators.

It was important to gain some idea as to the height to which the disturbance would travel, the distance at which a side effect could be observed, etc., and, as it was inconvenient to use smoke for these purposes. I made four sets of indicators, each consisting of a number of pieces of tissue paper about an inch square, hanging by thin silken fibres from long horizontal sticks. Three of these sticks were tied to the electric lamps, about 10 feet high ( $4\frac{1}{2}$  feet from the ceiling), while the fourth was mounted on a movable stand about 8 inches high, so that the indicators hung within an inch or two of the floor. Two of the high sets fronted the parapet at distances of about 18 and 32 feet from the tip of the fan resting on it; the third was about 20 feet from the parapet, in a diagonal line, making an angle of about  $45^\circ$  with its front (fig. 5).

Experiments with these indicators have established the following facts:—

(1) The air disturbance created by a stroke of the fan travels comparatively slowly, a single stroke with the army fan, in still air, taking 15 seconds to reach the indicators near the ground, 18 feet away.



(2) The maximum distance at which the disturbance produced by a single stroke is perceptible increases with the velocity and amplitude of the stroke.

(3) Each successive stroke, if the rate be above a certain minimum, carries the disturbance further, longitudinally, laterally, and vertically, till a certain maximum distance in each direction is reached.

(4) Below the minimum rate, which bears some sort of inverse ratio to the size of the fan, this cumulative effect is not produced; each stroke simply carries the disturbance to the maximum distance for a single stroke.

(5) The cumulative effect of the strokes increases with the rate of striking, and also with the amplitude of the stroke.

(6) The maximum distance at which the effect is perceptible in each direction increases with the size of the fan, with the rate of striking, and with the velocity and amplitude of the strokes.

#### *Nature of the Disturbance.*

With a view to examining the nature of the disturbance created by the fans, I have made a few experiments, by gently flapping smoke into clear air, with the following results :—

##### *1. Effect of a Single Stroke.*

After a single up-and-down stroke, the air issues from between the fan and the parapet as a vortex, rotating so that its upper boundary moves towards the fan, while as a whole it travels rapidly away from it. This vortex, the lines of which are horizontal, spreads out in an ever-widening curve, and, if no second stroke be made, it travels to a definite distance before it is dissipated. In raising the fan, however quickly, no movement towards it of the air in front of it seems to take place, but the air that rested on it after the last down-stroke is jerked upwards, while air from behind the fan comes in under the back between it and the parapet. The smallness of the air motion resulting from the raising of the fan is very remarkable when compared with the whirl caused by the gentlest down-stroke. If you place a delicate anemometer on the parapet quite close to the tip of an army fan, and jerk the fan upwards as quickly as you can, the vanes remain immovable, while they go careering round, however gently you let the fan fall. The reason is this. In raising the fan you create air pressure above the blade and behind the back, while, at the same time, a vacuum attempts to form between the whole fan and the parapet. If all parts of the fan were raised at once, the air from above and behind would rush round all the edges at once to fill in the vacuum. This does happen with an ordinary straight hingeless fan, and a flicker of the

anemometer vanes when such a fan is raised from rest shows it. But with my hinged fan the back is necessarily raised first, then the rigid part of the blade, and finally the end flap; consequently, before the tip is raised, the vacuum has already been filled from behind, the flow has become steady, and it is too small at any one place to affect even a very delicate anemometer.

A row of lighted candle-ends, held at the side of a fan in action, with the flames just above the striking surface, shows with great clearness the different directions of the air currents round that side of the fan. The flames near the front are blown outwards and quickly extinguished; the one near the back hinge flickers to and fro undecided; while those behind it are sucked in towards the fan. The rush of air from behind, during flapping, is distinctly felt as a cold wind over the ears and back of the head, as was first noticed by the soldiers who tested the fans at Chatham. It was the expectation of such a rush during the up-stroke, from analogy with my water experiments, that led me to try this method of driving off poisonous gases.

## *2. Effect of a Succession of Strokes.*

If a second stroke be made quickly enough after the first for the boundary of its vortex to come into contact with that of the first, a curious thing happens. The second vortex appears to burrow under the first, raising it bodily, and then to enter into and become enveloped in it, so that the two travel on together as one, pooling their energy, and reaching together a distance greater than the limiting distance for a single vortex. A third vortex will either catch up the other two before a fourth reaches it, or else the third and fourth together will catch up the first and second together; other things being equal, it is all a question of the rate of striking. In any case, the whole four together travel further than either a single one, or two together, or three together would do, and it is easy, therefore, to see how, after a succession of rapid strokes, the whole space in front and at the sides of the fan is traversed by a procession of vortices, that nearest the fan in the form in which it was shot forth, the others combined from two or three or more, the number in each combination increasing with the distance from the fan, but all rolling towards one final goal, namely, the huge vortex which gathers in the region where the energy from the constantly arriving stream of vortices only just balances the loss of energy through friction. The distance, in any one direction, of the further side of this vortex from the fan is the limiting distance to which the effect of the fan can reach in that direction, under the given conditions. With my little 1½-inch model fan, I found the limiting distance immediately in front of the fan to be about

10 feet—80 times its own length. With the army fan I have not yet found the limit.

*Summary.*

To sum up:—Roughly speaking, one of these fans, in action, divides the space around it into two regions, separated by a vertical plane passing through some line in the blade of the fan parallel to its tip. *From* the region behind the fan air is sucked, in *irrotational* motion, in all directions, *towards* the fan; *into* the region in front air is driven forth in *rotational* motion *away* from the fan. The fan cannot therefore be said to create a current in the ordinary sense of the word. What it does is to collect air from one wide region into a narrow space, and there to give it energy, both rotational and irrotational, by means of which it passes into another region, in which it moves through a longer, wider, and higher space than that from which it was collected. The fan is therefore a factory for turning still or comparatively slowly moving air into powerful vortices, which, by coalescing and reinforcing one another, are able to move through an enormous area, and to drive before them, in an ascending forward-moving stream, the air or gas that previously occupied the space through which they travel.

After the war, when practical problems are less insistent, I hope to enter more fully into the theory of this system of ousting undesirable gases by hurling vortices into them. For the present, it only remains for me to express my most grateful thanks to Mr. Greenslade for the patriotism and enthusiasm with which he came to my aid, devoting his holidays to the purpose. He did all the practical work of organising the tests of the fans and training soldiers to carry them out, both at Chatham and at G.H.Q., France; and later he went to all the four British armies in France to teach officers and N.C.O.'s what could be done with the fans and how the men should be trained to use them. He thus gave me invaluable assistance in a part of the work that I could ill have undertaken myself.

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*On the Colours of the Striae in Mica, and the Radiation from  
Laminar Diffracting Boundaries.*

By PHANINDRA NATH GHOSH, M.A., Lecturer on Optics in the Calcutta University.

(Communicated by Dr. Gilbert T. Walker, C.S.I., Sc.D., F.R.S. Received April 29, 1919.)

1. *Introduction.*

The phenomenon which forms the subject of this paper was briefly described in a preliminary communication in 'Nature,' made jointly by Prof. C. V. Raman and the author of this paper, accompanied by a short but suggestive note by Lord Rayleigh.\* It is observed when a clear sheet of transparent mica is placed in front of a good achromatic lens, and examined by the well-known Foucault "knife-edge" test, otherwise referred to also as the Topler "Schlieren" method. The arrangement is shown in fig. 1. White light from a slit, S (illuminated by a half-watt incandescent lamp of 100 C.P.), is incident upon the lens, L, which forms an achromatic image of the slit at some distance from the lens. A knife-edge, K, is put in the focal plane, and so placed that the light coming to a focus in the ordinary way is completely cut off.

The telescope, T, with its objective just behind the plane of the knife-edge, is pointed towards the lens, and is focussed on the surface of the mica (M.M.) placed immediately in front of the lens.

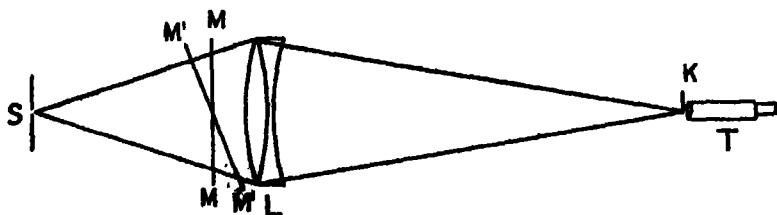


FIG. 1.

The mica, as a whole, being optically good, remains invisible, but a few more or less irregular striæ or lines on its surface are generally visible, and these are seen in the apparatus as brilliant and vividly coloured lines of light, the colours being usually different for different striæ. If the mica be turned about an axis in its own plane (*e.g.*, into the position M'M' shown in the

\* "On the Colours of the Striae in Mica," 'Nature,' November 14, 1918.

figure), the colours change in a remarkable manner. For instance, a stria that appears in the normal position as a fine golden yellow line, on rotation of the plane gradually changes colour to purple, then to blue, then to green, and finally to the yellow colour. The phenomenon is best seen when the stria under observation runs more or less parallel to the direction of the slit S in the illuminating apparatus.

It is proposed in the present paper to consider these effects in some detail, and to describe some further observations made by the writer since the publication of the preliminary note in 'Nature.'

## 2. *Nature of the Striæ.*

The nature of the optical irregularities that constitute the striæ in mica may be readily determined. One method of settling the question is by the observation of Haidinger's rings in mica, which have been recently very fully studied by Chinmayanandam.\*

The mica is placed about an inch in front of, and parallel to, a sheet of white cardboard, which is illuminated on the side facing the mica by the light of a Cooper-Hewitt lamp. The reflected system of interference rings is observed through a small hole in the centre of the cardboard placed close to the eye, the rear face of the cardboard being blackened to avoid extraneous light. When the mica is moved in its own plane, it is noticed that the first few rings expand or contract when a stria passes over the system. The rings also appear distorted and irregular so long as the stria remains in the field of vision.

The foregoing observation clearly indicates that a stria is the boundary separating regions in the mica having slightly different thicknesses. Its exact outline is, however, better seen in monochromatic light, when the eye is focussed on the surface of the mica, which has then, of course, to be removed to some distance from the observer. As described by Lord Rayleigh in his note "On the Regularity of Structure of Actual Crystals,"† the surface then appears divided into patches of different intensities, the patches themselves appearing uniform and the boundaries sharp to an eye focussed on the plate. It is readily verified by examination of a number of specimens that it is these boundaries which appear as striæ when mica is examined by the knife-edge test. The striæ are apparently formed by the unevenness of the splitting of the mica. This is indicated by the fact that the striæ in the pieces formed by dividing a sheet of mica into two, are exact counterparts of each other.

\* 'Roy. Soc. Proc.,' A, vol. 95 (1918).

† 'Phil. Mag.,' vol. 19, pp. 98-99 (1910); 'Scientific Papers,' vol. 5, 342, pp. 536-539.

In the experimental work described in this paper, the differences of thickness on the two sides of the striæ were determined with the Jamin interferometer. When this difference is considerable, it is rendered evident in ordinary day-light on putting the mica between crossed nicols, by the difference of tint seen on the two sides of the boundary.

### 3. *Laminar Diffraction and the Colours Observed in the Foucault Test.*

The writer has found an interesting relation between the colours of the striæ, as seen in the Foucault test, and the ordinary phenomena of laminary diffraction. When white light from a point source passes through a sheet of mica, the non-uniformity in the thickness of the plate and the consequent differences in the retardation produced by it, disturb the wave propagation, and each stria in the mica produces in the field of transmitted light a system of diffraction fringes which follow the general outline of the stria in their shape. These fringes may be readily observed through a low-power eye-piece placed behind the mica some distance from it. Each system is more or less exactly symmetrical about its central fringe, which is strongly coloured. The writer has found that the colour of any stria, as seen in the Foucault test, is *exactly complementary* to the colour of the central fringe in the laminary diffraction pattern produced by it. For instance, a stria that at normal incidence appears golden-yellow in the Foucault test, produces a laminary diffraction pattern with a greenish-blue central fringe. The complementary character of the two phenomena holds good also when the mica is held obliquely in the path of the incident light. For instance, on rotating the mica, the colour of the central fringe of the diffraction pattern produced by the striæ noted above changes from greenish-blue to green, then to red, and finally again greenish-blue. For any given wave-length, when the central fringe is bright, the stria appears dark, and *vice versâ*.

The foregoing observation enables us clearly to see the relation between the luminosity of the striæ, as observed in the Foucault test, and the relative retardation of the wave-front on the two sides of the boundary which the stria represents. When the difference in the retardation is an exact integral multiple of a wave-length, the wave-front emerges from the plate practically without disturbance, and it follows from what has been said above that the luminosity of the stria in the Foucault test for the particular wave-length must vanish. Similarly, when the relative retardation is an integral number of wave-lengths plus half a wave-length, the central fringe in the laminary diffraction pattern would be perfectly black, and the luminosity of the stria in the Foucault test would then be a maximum for the wave-length considered.

The striæ only appear coloured when the difference of retardation on the two sides of the boundary does not exceed a few wave-lengths. With greater thicknesses the striæ appear luminous, but white. In these cases, however, by putting a prism at the eyepiece end of the observing telescope, the image of each stria may be seen drawn out into a spectrum, crossing which we have two, three, four, or even larger number of dark bands, representing wave-lengths for which the luminosity of the stria is zero. The changes in the position of the bands in the spectrum produced by tilting the mica about an axis in its own plane may also be readily noticed.

#### *4. Attempts to Reproduce the Phenomenon by Etching Glass Plates.*

Mica, with its transparency and the ease of its natural cleavage, is by far the most suitable material for observing the colours of laminar boundaries in the Foucault test. Suitable pieces of selenite have also been found to show the phenomenon, though in a much less striking manner. Cleavage rhombs of calcite also occasionally show coloured striæ. It was thought that it would be of interest to see if the phenomenon could be reproduced artificially by etching part of a glass surface with very dilute hydrofluoric acid, the other part being protected by a coating of wax, which is subsequently removed. Several attempts were made by this method, as also by coating part of a glass surface with very thin films of collodion or celluloid, but the results obtained were not encouraging. A plate thus coated or etched generally shows the boundary as a luminous line, more or less perfectly white, and with hardly any trace of colour. Only in one case was anything like a definite indication of colour obtained, but this was a very poor contrast with the gorgeous displays furnished by mica in the Foucault test. The failure to obtain colours in these cases appears to be due to the want of suddenness in the change of thickness at the boundary formed by etching or coating a plate of glass.

Obviously, in the case of a gradual slope, we have a less simple case of laminar diffraction than when we are dealing with a sudden change of thickness. The principal differences are that, in the former case, the laminar diffraction occurs from an area of finite width, and there is also a distinct element of asymmetry; whereas, in the latter case, the scattering of the light by the boundary must obviously occur in a more or less symmetrical manner. That there is actually an asymmetry of the kind indicated in the case of etched or coated glass plates can be shown experimentally. Referring to the diagram of the apparatus (fig. 1), it will be seen that it is open to us to put the knife-edge in the focal plane either from above or below. In the case of mica this is found to make no appreciable

difference, so long as the area of the objective of the observing telescope not covered by the knife-edge is the same in both cases. But with the etched or coated glass plates a very great difference is found in the luminosity of the stria according as the knife-edge is put in from above or from below. Apparently, an appreciable area of the wave-front is retarded in an unsymmetrical manner, and this leads to a marked difference in the intensity of the diffracted light on the two sides of the focus.

The difficulty in obtaining a perfectly sharp boundary by etching a plate of glass is also shown by observations of the laminar diffraction pattern produced by a point source of light with a plate so etched. The diffraction fringes show a marked difference of intensity on the two sides of the shadow of the boundary.\*

The dependence of the configuration and intensity of the laminar diffraction fringes on the nature of the transition at the boundary would appear to furnish an interesting field for study.

#### *5. Apparent Doubling of the Striae by Phase-Reversal.*

An interesting effect is noticed if, instead of the knife-edge ordinarily used in the Foucault test, we substitute a central stop, which cuts off the light brought to a focus by the achromatic lens, but allows the light on *both* sides of the focus diffracted by the striae to enter the object-glass of the observing telescope. Each of the striae in the mica then appears *doubled*, a fine perfectly black line appearing in the position of the striae, and a bright coloured image of the stria on either side of it. The effect is somewhat similar to that recently described by Banerji† in regard to the luminous boundaries of diffracting apertures, except that, in the present case, the fringes on either side of the central black line are *coloured* and not white, as in the case of opaque screens. The explanation of the effect is analogous to that given by Banerji, viz., that the light diffracted by the stria and reaching the focal plane of the achromatic lens is in opposite phases on the two sides of the focus. We may regard each stria as giving out two streams of diffracted radiation, one on each side of the direction of the regularly transmitted rays, and these two streams are in opposite phases. Consequently, when they both enter the observing telescope, they interfere, and give zero illumination at the position of the image of the boundary, and luminous fringes on either side of it. The *intensity* of the radiation

\* The asymmetry can be clearly seen in a photograph of laminar diffraction by an etched glass plate reproduced in R. W. Wood's 'Physical Optics' (1914 edition, p. 251), though Wood does not draw attention to this feature.

† S. K. Banerji, 'Phil. Mag.', January, pp. 110-123 (1919).



from the laminar boundary depends, of course, upon the relative retardations of the wave-front on the two sides of the boundary, and is a maximum when this retardation is half a wave-length plus any integral number of wave-lengths, and a minimum when the retardation is an integral number of wave-lengths.

### 6. Mathematical Theory.

*Laminar Diffraction.*—A rigorous treatment of the diffraction of light by a laminar boundary does not appear to have been given, and would obviously be difficult. *Prima facie*, it may be expected that the boundary would scatter light in all directions, the intensity of the scattered radiation depending in a somewhat complicated manner upon the angles of incidence and diffraction, upon the difference in thickness and the nature of the transition at the boundary, upon the wave-length and refractive index or indices of the medium, and also upon the state of polarisation of the incident light. In dealing with the Foucault test, however, we are practically concerned with small deviations, that is with the effects observed in the directions not far removed from that of the incident waves. This limitation simplifies the problem, as the ordinary Fresnel-Kirchoff treatment of diffraction phenomena then becomes applicable. If the difference of thickness at the laminar boundary does not exceed a few wave-lengths and the transition is more or less sudden, it may be legitimately assumed that the wave-front after passage through the plate consists of two parts, one retarded with respect to the other by a certain interval.

The difference  $2\rho$  of the retardation of the two parts of the wave-front is  $(\mu-1)e$  if the plate be held normally,  $e$  being the difference of thickness. For oblique incidence, it is easily shown that  $2\rho = e(\mu \cos r - \cos i)$ , which may also be written in the form  $e(\sin(i-r)/\sin r)$ , or  $\mu e \sin(i-r)/\sin i$ . From this, it is clear that the difference of retardation increases with the obliquity.

Elementary theory shows that directly behind the laminar boundary the intensity is a maximum or minimum according as  $2\rho$  is an even or an odd multiple of half the wave-length of the light used. In addition on both sides of this line there are diffraction fringes symmetrical about the line.\*

*Theory of Foucault Test.*—A stricter theory which takes into account the convergence of the wave and the limitation of its aperture in passing through the achromatic lens and also the limitation in the focal plane of the lens by knife-edge and by the object glass of the observing telescope, is given in a recent paper by Lord Rayleigh.†

\* Wood's 'Optics,' Chap. VII, Section : Diffraction by Thin Laminae.

† 'Phil. Mag.,' February, p. 174 (1917).

He considers the case of the retardation produced by a discontinuous laminar boundary, and shows that the direction of the boundary would appear strongly marked by an excess of brightness.

It seems unnecessary to repeat here the detailed analysis given by him to which the reader might be referred. Lord Rayleigh's results may, however, be quoted in order to illustrate and explain the phenomena actually observed with mica. The discontinuous boundary being visible in the centre of the field of the observing telescope, the expression of intensity for the direction of the boundary takes the following form for a given wave-length  $\lambda$ :

$$I(0) = \left[ \cos \frac{2\pi\rho}{\lambda} \left\{ 2\text{Si} \frac{2\pi\theta\xi_2}{\lambda} - 2\text{Si} \frac{2\pi\theta\xi_1}{\lambda} \right\} + \sin \frac{2\pi\rho}{\lambda} \left\{ 2 \log \frac{\xi_2}{\xi_1} + 2\text{Ci} \frac{2\pi\theta\xi_1}{\lambda} - 2\text{Ci} \frac{2\pi\theta\xi_2}{\lambda} \right\} \right]^2, \quad (1)$$

where  $\theta$  is the semi-angular aperture of the achromatic lens;  $\xi_1$  and  $\xi_2$  are the lower and upper limits of the opening in the focal plane.

We may now proceed to show that the colours of the striae, as seen in the Foucault test, are virtually independent of the position of the knife-edge in the focal plane, provided it be sufficiently advanced to cut off the bulk of the light coming to a focus in the ordinary way. The intensity of luminosity as given by (1) depends on the magnitude of  $\xi_1$  and  $\xi_2$ .

When  $\xi_2$  is large,  $\text{Si}(2\pi\theta\xi_2/\lambda)$  can be taken to be  $\frac{1}{2}\pi$  and  $\text{Ci}(2\pi\theta\xi_2/\lambda)$  may be neglected.

We may then write

$$I(0) = \left[ \cos \frac{2\pi\rho}{\lambda} \left\{ \pi - 2\text{Si} \frac{2\pi\theta\xi_1}{\lambda} \right\} + \sin \frac{2\pi\rho}{\lambda} \left\{ 2 \log \frac{\xi_2}{\xi_1} + 2\text{Ci} \frac{2\pi\theta\xi_1}{\lambda} \right\} \right]^2.$$

Further, if  $\xi_1$  be small compared with  $\xi_2$ ,  $\log(\xi_2/\xi_1)$  is large; and provided  $\xi_1 > (\lambda/2\theta)$ , i.e., if the knife-edge be sufficiently advanced to cut off at least the whole of the central band in the diffraction pattern in the focal plane, the coefficient of  $\sin(2\pi\rho/\lambda)$  within the brackets practically reduces to the quantity  $2\log(\xi_2/\xi_1)$ , which is independent of the wave-length, and is also much larger than the coefficient of  $\cos(2\pi\rho/\lambda)$ .

Hence it follows that when the knife-edge is sufficiently advanced in the focal plane to cut off the bulk of the light coming to a focus, any further movement of the knife-edge which increases  $\xi_1$ , merely reduces the apparent intensity of the luminosity of the laminar boundary, but does not alter its colour. This is, however, not true if  $\xi_1$  be *small*, that is, if the knife-edge does not completely cut off the central band of the diffraction pattern for all the wave-lengths in the visible spectrum. For the Ci function has then a large value and is not negligible in comparison with  $\log(\xi_2/\xi_1)$ , and the light

of longer wave-lengths which comes to a focus and escapes being cut off by the knife-edge, produces an appreciable alteration in the colour of the striæ as seen in the observing telescope. If the coefficient of  $\cos^2(2\pi\rho/\lambda)$  be sufficiently small, the colours of the striæ are practically determined by the variation of  $\sin^2(2\pi\rho/\lambda)$  with the wave-length,  $2\rho$  being the relative retardation on the two sides of the laminar boundary. The intensity is a maximum for those wave-lengths for which this retardation is half a wave-length plus any integral number of wave-lengths.

In any case, the colour of the striæ can be calculated for any given value of  $\rho$ , using the Maxwell colour triangle in a manner similar to that used by Lord Rayleigh in discussing the interference colours of thin plates.\*

The expression given by Lord Rayleigh also serves to explain the apparent doubling of the striæ described in Section 5 above. In this case we have two apertures symmetrically placed extending from  $\xi_1$  to  $\xi_2$  and  $-\xi_1$  to  $-\xi_2$ , and the expression for the vibration in the focal plane may then be written as

$$2 \cdot \sin T \left[ \cos \frac{2\pi\rho}{\lambda} \left\{ \text{Si} \frac{2\pi\theta}{\lambda} \left(1 + \frac{\phi}{\theta}\right) \xi_2 - \text{Si} \frac{2\pi\theta}{\lambda} \left(1 + \frac{\phi}{\theta}\right) \xi_1 \right. \right. \\ \left. \left. + \text{Si} \frac{2\pi\theta}{\lambda} \left(1 - \frac{\phi}{\theta}\right) \xi_2 - \text{Si} \frac{2\pi\theta}{\lambda} \left(1 - \frac{\phi}{\theta}\right) \xi_1 \right\} \right] \\ + 2 \cdot \cos T \left[ \sin \frac{2\pi\rho}{\lambda} \left\{ \text{Si} \frac{2\pi\phi}{\lambda} \xi_2 - \text{Si} \frac{2\pi\phi}{\lambda} \xi_1 - \text{Si} \frac{2\pi\theta}{\lambda} \left(1 + \frac{\phi}{\theta}\right) \xi_2 \right. \right. \\ \left. \left. + \text{Si} \frac{2\pi\theta}{\lambda} \left(1 + \frac{\phi}{\theta}\right) \xi_1 + \text{Si} \frac{2\pi\theta}{\lambda} \left(1 - \frac{\phi}{\theta}\right) \xi_2 - \text{Si} \frac{2\pi\theta}{\lambda} \left(1 - \frac{\phi}{\theta}\right) \xi_1 \right\} \right].$$

In the direction of the boundary, *i.e.*, when  $\phi = 0$ , the coefficient of  $\sin 2\pi\rho/\lambda$  vanishes, and

$$I(0) = 16 \cos^2 \frac{2\pi\rho}{\lambda} \left[ \text{Si} \frac{2\pi\theta}{\lambda} \xi_2 - \text{Si} \frac{2\pi\theta}{\lambda} \xi_1 \right]^2,$$

which gives very small values for the intensity. When  $\phi$  is slightly less or greater than zero, we get large values for the intensity; showing that the striæ appear doubled with a dark line in the centre. Further, it is found that in passing through the direction  $\phi = 0$ ,  $\sqrt{I}$  changes sign, thus showing that the phase of the diffracted waves differs by  $\pi$  on the two sides of the boundary.

### 7. *Experimental Tests of the Theory.*

From a knowledge of the difference of retardation at a stria (as determined with the Jamin interferometer), the colour it should show in the Foucault test may be computed, using the method of the Maxwell colour

\* 'Edinburgh Transactions,' 33, pp. 157-170; 'Scientific Papers,' vol. 2, pp. 498-510.

triangle, and checked with that actually observed. This was done for the cases noted below, and good agreement was found.

$2p$ .	Colour actually observed.
$456 \times 10^{-7}$ cms.	Golden yellow.
$527 \times 10^{-7}$ cms.	Purple.
$631 \times 10^{-7}$ cms.	Blue.

A quantitative test of the formulæ for the case in which the mica is held obliquely, is possible by using approximately monochromatic light for illuminating the slit, and finding the angle through which the mica should be rotated from the normal position to extinguish the luminosity of the stria. This should occur when the retardation for the oblique position is equal to an integral number of wave-lengths of the light used. The test was actually made by putting a red glass plate in front of the illuminating slit having a transmission region from about 6300 A.U. to 6500 A.U. in the spectrum, and turning the mica till the stria under observation vanished. This was done for the two cases noted below:—

$2p$ (for normal position).	Rotation necessary for extinction.			
	Observed.		Calculated.	
$456 \times 10^{-7}$ cms.	58	10	57	30
$527 \times 10^{-7}$ cms.	49	5	48	30

According to the theory set out above, the colour of a stria is determined by the difference in the retardation of a wave-front passing on either side of it. If the mica be immersed in a cell containing liquid, this retardation, which in air is  $(\mu-1)e$  decreases to  $(\mu-\mu')e$ , where  $\mu'$  is the refractive index of the liquid, and we should accordingly expect to find that the colour of stria as seen in the Foucault test should also alter. This is confirmed in experiment, and it is also noticed that striæ which are luminous but white in air (being too thick to show colour) appeared coloured when immersed in a cell containing water. As a specific instance may be quoted the case of a stria which in air appears green, and immersed in water appears violet.

The refractive index of water being taken as 1.33, this observation is found to be in quantitative agreement with theory.

### 8. Summary and Conclusion.

The paper describes the results of a fuller investigation of the phenomenon of the coloured striæ observed when mica is examined by the Foucault test,

described by Prof. C. V. Raman and the present author in a preliminary communication in 'Nature.' The following are the principal results obtained which have been discussed in the light of mathematical theory.

(a) The striæ are shown by an examination of the Haidinger's rings in mica (and also otherwise), to be the boundaries between parts having slightly different thicknesses.

(b) The colour of any stria as seen in the Foucault test is complementary to the colour of the central fringe in the laminary diffraction-pattern produced by it.

(c) The colours are altered by holding the mica obliquely, or by immersing it in a cell containing liquid.

(d) The luminosity of a stria in the Foucault test is approximately a maximum when the phases of the wave-front after passing through the plate on the two sides of the stria are opposite, and practically zero when the phases are identical.

(e) Attempts to reproduce the phenomenon by etching glass plates with dilute hydrofluoric acid were not very successful, owing apparently to a want of sufficient sharpness in the boundary thus produced. This is indicated by the fact that such a plate shows distinct *asymmetry* with reference to the direction of the incident light, both in the Foucault test and in laminar diffraction.

(f) The striæ in mica appear doubled (with a black line in the centre), when the light coming to a focus is screened in a symmetrical manner, instead of by a knife-edge as in the Foucault test.

It is proposed at an early opportunity to continue the work, especially in regard to the colour and polarisation of the light diffracted through *large* angles by the striæ, and also to make a fuller study of the cases in which light is diffracted by a laminar boundary in an unsymmetrical manner.

The experimental work described in this paper was carried out in the Palit Laboratory of Physics, and the writer wishes to express his cordial thanks to Prof. C. V. Raman with whom he was associated in the preliminary observations of the colours of the striæ in mica, and at whose suggestion he undertook the detailed investigation of the phenomenon. He also wishes to thank Dr. Gilbert Walker, F.R.S., for his kind interest in the research and for bringing it before the Royal Society.

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*Diffusion of Light by Rain, Cloud, or Fog.*

By A. MALLOCK, F.R.S.

(Received June 11, 1919.)

The effects of the diffusion of light by small particles may broadly be divided into two classes, according as the linear dimensions of the particles are large or small compared with the wave-length of the light. In the present note only the first of these classes is considered.

Rain, cloud and fog all consist of small spheres of water distributed at random in the air, and with very different degrees of concentration. Their linear dimensions may exceed a tenth of an inch, in the case of rain, or be less than a thousandth of an inch in cloud and fog.

The action of individual spheres on incident light is given in the theory of the rainbow. Any direct ray from the source of light is scattered but not uniformly, partly by external and partly by internal reflection; but when so many drops are contained in a given volume that none, or only a very few of them, receive any direct light, each drop acts as a separate source, scattering such light as it receives from the others in every direction uniformly.

Let a source of light be situated within an indefinitely extended cloud, and let the drops be perfectly transparent, so that there is no real loss of light by absorption, and consider the illumination at such a distance from the source that no direct rays operate. Since the total quantity of light passing through every spherical surface about the source is constant, it is clear that the illumination will vary inversely as the square of the distance from the source, and will be the same as the brightness of a small perfectly white plane surface (which may be called a proof-plane) at the same distance when fully exposed to the direct rays.

As to the rate at which direct illumination is reduced as the distance increases; suppose that  $n$  drops of diameter  $c$  are contained in the volume  $a^3$ . If these were all placed side by side they would stop all direct rays, if  $n = a^3/c^3$ ,\* but as in reality they are scattered at random through  $a^3$ , some will screen others, and it becomes a question of probabilities to determine how far this screening action increases the chance of direct radiation reaching

\* Since the drops are circular in section, and since a hexagon is the regular figure most nearly approaching a circle which can cover an area without overlap, the actual number of drops required to cut off all direct rays will exceed  $a^3/c^3$  in the ratio of the area of a circle to that of the inscribed hexagon, but as in the present note the order of magnitude rather than its exact value is considered, it is unnecessary to introduce this coefficient.

the far side of the volume  $a^3$ . The problem is the same as the determination of the number of empty spaces which would probably be left on an area  $a^2$ , divided into  $n$  equal squares, when  $n$  things were thrown on it at random.

The  $n$  things can be made into parcels in various ways, and these may fall on any combination of the  $n$  areas taken 1, 2, 3, etc., at a time.

Questions of probability are rather notoriously liable to be wrongly estimated, but I believe that in this case the most likely result is that half the squares will be empty. Also, that in the case of  $mn$  things being thrown, the probable number of empty squares is  $1/2^m$ .

It may be noticed that, however small the quantity of water per unit volume, it is always possible to divide that quantity into a sufficient number of drops to cover the unit area,\* but in the cases here considered, the permissible smallness is limited by the condition that the diameter must not be less than, say, ten wave-lengths, or roughly  $1/5000$  of an inch, and since the atmosphere at ordinary temperature contains about one part in 100,000 of water vapour, if this were condensed in the form of spheres  $1/5000$  inch in diameter it would require a column of air 20 inches long to contain a sufficient number of drops to stop, when placed side by side, all direct radiation, or to stop half the direct light when distributed at random in the same volume.

If the length of the column (or thickness of the stratum) which halves the direct light be denoted by  $l$ ,  $l$  may be taken as the coefficient of transparency of any collection of drops of constant size.

For drops a tenth of an inch in diameter  $l$  would be 10,000 inches, and generally, the same obstruction to direct light occurs when  $l$  varies as the diameter of the drops. On the assumption that no light is lost in the act of reflection, the diffused light at a distance  $ml$  from the source will vary as  $1-2^{-m}$ . Thus, in the case of an unlimited sheet of cloud or shower illuminated by the sun,† the brightness of the proof-plane, if it faces the source of light, is always constant in whatever position in the cloud it is observed, but when within only a small multiple of  $l$  from the boundaries (front or back), part of the illumination, or loss of illumination, is by direct radiation, and part by diffused light or its deficiency. In such positions the

\* The same proposition shows either that stars cannot be uniformly scattered through all space or that light is in some way lost in transmission, or that the greater number of the stars give no light, or again, more improbably, that visible space is bounded by something impervious to light. Unless one or other of these alternatives were true, starlight would be brighter than sunlight in nearly the same proportion as daylight from white clouds exceeds the light from the full moon.

† Or when the distance from the source is great compared to the thickness of the cloud sheet.

brightness is affected by the angle which that normal to the proof-plane makes with the direct rays.

If a cloud contained a source of light and was also surrounded by a perfect reflector, the illumination of the enclosure would be everywhere constant and of the same intensity as the source itself.

The diffusion of light by cloud, etc., follows the same laws as the diffusion of heat in a nearly perfectly conducting body, and with this restriction regarding conductivity the same propositions apply to both as far as steady flow is concerned, but since in the case of light the rate of conduction is the velocity of light, the variation of flow in terms of time has no practical importance in this connection.\*

The diffusion of light and heat in a perfectly conducting sphere or in a long prism may, for example, be compared. If the sphere contains the source the brightness of the proof-plane when turned to face the source is everywhere inversely as the square of the distance from the source, but that part of the intensity, however, which depends on diffusion is modified as the point of observation approaches within a few multiples of  $l$  from the surface. In the analogous case of the diffusion of heat, similar changes of temperature would be found if the proof-plane were backed by a substance impervious to heat. When close to the surface, and with its back to the source, the intensity depends entirely on diffusion from that part of the sphere which lies between the proof-plane and the boundary facing it, which part is itself losing energy by direct radiation into space. If the proof-plane is gradually turned so as to face the source, the temperature at the same time rises gradually to its full value.

The same form of integrals which determine the intensity for an internal source apply when the source is external, but in either case it would be difficult to compare the results of experiment with theory. Such a comparison, however, for a prism or a bar, one end of which was exposed to a constant source of light, or kept at a constant high temperature while loss by radiation was going on from the sides, could easily be made. The effects of a cloud could be copied by a tube containing an emulsion of colourless oil and water lit from above. The intensity at the section distant  $x$  from the surface would be proportional to  $e^{-kx}$ , and would be nearly uniform across that section if the lateral dimension of the bar were small compared to  $l$ . In an actual experiment the loss of light by

\* Fourier (*Traité de Chaleur*, chap. IX, p. 430) recognises two coefficients of conduction, which he calls the "pénétrabilité" and the "perméabilité" of the substance. The first relates to radiant heat, and the second to ordinary conduction. In the diffusion of light the "pénétrabilité" and "perméabilité" are identical.



reflection and absorption would have to be taken into account, and would be represented in the exponent by an additional term depending on the properties of the fluids forming the emulsion, or of the bar.

Returning to the subject of the diffusion of light by rain, etc., the following Table shows the effect of a shower or cloud in obscuring the direct light of a distant source.

The difficulty of seeing objects through a stratum not many times  $l$  in thickness depends chiefly on the diminished contrast between light and shade caused by diffusion, and not on loss of definition; the sun, for instance, can often be seen perfectly defined through a layer of cloud which reduces its light to a very small fraction of its unshaded intensity.

The quantities used in the computation of the Table are:—

$a$  = Unit length.

Column I.  $c$  = Diameter of drop.

„ II.  $n = a^3/c^3$  = number of drops in volume  $a^3$  requisite to halve the directly transmitted light.

„ III.  $l$  = Length in inches of a column of the cloud of section of the cloud of section  $a^2$  which contains  $n$  drops.

„ IV.  $l$  = Ditto in feet.

$L$  = Thickness of the cloud in line of sight.

$m = L/l$ .

$Q$  = Water-content of cloud in volume  $a^3$ .

$I_0$  = Brightness of proof-plane exposed to direct light from the source (supposed distant).

$I_L$  = Ditto. Due to direct light at distance  $L$  from the lit boundary of the cloud.

„ V.  $N$  = Number of drops per unit volume of cloud.

„ VI.  $D$  = Average distance between the drops.

These are related as follows:—

$$(1) n = a^3/c^3, \quad (2) l = c/Q, \quad (3) m = L/l, \quad (4) I_L = I_0 \times 2^{-m}, \quad (5) N = n/l, \\ (6) D = N^{-1/3}.$$

It has been assumed (as a not impossible proportion) that  $Q = 1/100,000$ .

Table I.

I.	II.	III.	IV.	V.	VI.
(c).	(n).	(l).	(l).	(N).	(D).
inches.		inches.	feet.		inches.
0·1	100	10,000	830	0·01	4·6
0·08	164	8,000	666	0·0204	3·65
0·06	285	6,000	500	0·0475	2·71
0·05	400	5,000	417	0·080	2·32
0·04	625	4,000	333	0·156	1·82
0·02	2,500	2,000	166	1·25	1·045
0·01	10,000	1,000	83	10	0·483
0·008	16,400	800	666	20·5	0·365
0·006	28,500	600	50	47·5	0·275
0·005	40,000	500	41·7	80	0·232
0·004	62,500	400	33·3	366	0·140
0·002	250,000	200	16·6	1,250	0·092
0·001	1,000,000	100	8·3	10,000	0·022

There is an obvious connection between the opacity of a shower and the rainfall; for the size, concentration, and velocity of the falling drops govern the latter, while the opacity to direct rays depends on the size and concentration only.

If  $\eta$  is the rate of rainfall and  $v$  the velocity of the drop,  $vc = \eta l$ ; and it may be noted that a rainfall of 1·15 in. per day is equivalent to  $w = 1/100,000$  in. per sec.

As far as I know,\* there are no experiments or observations on the size of the drops which constitute rain, cloud, or fog (although when the drops are very small some evidence on this point can be got from the subtense of the halos they produce), nor has the velocity of moderate sized rain drops been measured. The theoretical work of Stokes, in which viscosity is supposed to control the retardation, to the exclusion of the inertia of the surrounding air, applies only to very minute particles.

If the equation  $vc = \eta l$  is applied to the results given in the Table, it will be seen that  $Q$  has been greatly overestimated, and that in the case of rain

\* Since this passage was written my attention has been drawn to the following papers, which bear on the subject:—(1) Lenard, 'Meteorologische Zeitschrift,' 1904, p. 249; (2) Schmidt, 'Meteorologische Zeitschrift,' 1909, p. 183; (3) Wiesner, 'Vienna Akad. Sitzber.,' vol. 104, I, p. 1397 (1895). Lenard and Schmidt give experimental determinations of the velocity of falling drops in terms of their diameter. The methods employed were quite different, but the results are in substantial agreement. Schmidt compares his own and Lenard's values with those given by a formula of the type  $v = 1/\sqrt{1/Ar^2 + 1/B}/r$  ( $v$  = velocity,  $r$  = radius of drop). The constants have been chosen so as to make the formula agree with experiment for small values of  $r$ . As  $r$  increases there is a considerable and growing divergence between the  $v$  of the formula and the  $v$  actually measured.

the drops cannot form anything like  $1/100,000$  of the total volume. For example, though the limiting velocity of drops a tenth of an inch in diameter has not been measured, ordinary observation of heavy rain will show that it is not less than 10 ft. per sec., and thus with  $Q = 10^{-5}$  *w* would be not less than  $1.2 \times 10^2 \times 10^{-1}/10^4$  in. per sec., *i.e.*, 100 in. per day. There are no measures, as far as I know,\* of rainfall per second, or for any short intervals, but it is not impossible that a rate of 10 in. per day, or even more, might be reached occasionally. It may safely be inferred, however, that even in the heaviest rain  $Q$  is rarely as great as  $10^{-6}$ .

The case is rather different for fog and mist, where the velocity of the drops is very small, but even when a fog is so dense as to make a street-lamp only just visible at a distance of 10 ft. (the densest white fog in my experience) it will be found that either the drops must have been much less than a thousandth of an inch in diameter or  $Q$  much less than  $10^{-6}$ .

## BAKERIAN LECTURE: *A Study of the Line Spectrum of Sodium as Excited by Fluorescence.*

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(Received June 17,—Lecture delivered June 19, 1919.)

### [PLATE 5.]

	CONTENTS.	PAGE
§ 1.	Introductory.....	272
§ 2.	The Sodium Vapour Lamp .....	274
§ 3.	Radiation of the Lamp. Minute Structure of the D Lines .....	276
§ 4.	Resonance with D Light .....	277
§ 5.	Breadth of the Resonance D Lines .....	278
§ 6.	Resonance Radiation at the First Ultra-violet Line .....	280
§ 7.	Resonance and the Zeeman Effect .....	281
§ 8.	Stimulation of D Light by Excitation at the First Ultra-violet Line .....	282
§ 9.	The Two D Lines Separately Considered .....	283
§ 10.	Polarisation Experiments .....	284
§ 11.	Connection between D Lines and the Band Spectrum.....	285
§ 12.	Summary of hitherto unpublished Experimental Work .....	286

### § 1. *Introductory.*

It was recognised in the early days of spectrum analysis by Stokes and Kirchhoff that the absorption of light by a sodium flame or by sodium vapour

\* Wiener gives an account of the rainfall at Buitenzorg, and has measured the rate of rainfall over intervals of 5 to 15 minutes. In one case the rate of rainfall of 3.27 metres per day (nearly 48,000 inches per year) was recorded as lasting over 15 minutes.

was conditioned by resonance of the vibrating sodium molecules to that period in the exciting light which was removed. In more recent days our knowledge of these phenomena has been much extended by E. Wiedmann, and later, R. W. Wood, who showed that the absorption just mentioned was accompanied to some extent by lateral re-emission.\* L. Dunoyer has also made important observations. This is the phenomenon known as resonance radiation.

[Since this paper was written I have to lament the death of my beloved father, Lord Rayleigh. I found the following rough memorandum, dated September, 1897, among his papers, not put away carefully, but in a pile of letters and pamphlets of no value. It was written long previously to my own interest in the subject, and I think he had quite forgotten having considered the matter; at all events, he never referred to it when I showed him some of my own experiments. The memorandum runs thus:—"A moderately fed soda flame stops light of D quality incident upon it. This may be seen to some extent with sunlight, but better with electric arc, or perhaps with another and brighter soda flame. What is the nature of this stopping? It is generally spoken of as absorption. But this seems unlikely. It must be a molecular operation. If the molecule in the Bunsen shines on excitation, how can it fail to do so as the result of energy of the right sort already falling upon it, and certainly operative upon it? It seems more likely that the energy is re-radiated without absorption, *i.e.*, that the light is *scattered*. If so, it would probably be scattered as from small particles of the ordinary sort with polarisation effect."—July 21, 1919.]

The range of conditions for resonance radiation is much more restricted than for absorption. Had it been otherwise, the discovery would not have been so long deferred. Absorption is not interfered with—indeed, the absorption lines are much broader and easier of observation, when the sodium vapour is enormously diluted with foreign gases, as, for instance, in a Bunsen flame. The causes of this broadening are not yet clear, but it is certain that the lines become very much narrower when the sodium is *in vacuo*, and it is under these conditions that the resonance radiation makes its appearance. Evidently the same interaction with the surrounding gas which broadens the absorption line in some way conditions the disappearance of the resonance radiation.

\* For an account of Wood's investigations prior to 1912, see his 'Physical Optics,' 2nd ed., and papers in the 'Philosophical Magazine' since that date. Dunoyer's more important papers will be found in 'Le Radium,' vol. 9, May, 1912, and 'Journal de Physique,' January, 1914. My own earlier observations will be found in 'Roy. Soc. Proc.,' A, vol. 91, pp. 389 and 511 (1915). They are summarised in the present paper, which also contains new material.

Since the absorption lines are extremely narrow under the conditions which are favourable for observing resonance radiation, and since only the absorbed radiations can be effective, it results that for good efficiency the source employed to stimulate the resonance should be one giving extremely narrow bright lines. Light belonging to any other part of the spectrum is worse than useless, for it is inevitably diffused to some extent by the walls of the vessel used, and tends to mask the effects to be looked for.

The salted Bunsen flame is a very poor source of radiation for these experiments, because of the breadth of the lines. As Dunoyer has shown, it works to best advantage when sparingly supplied with salt, for when salt is freely supplied the lines become broader, and useless radiation outside the effective region of the spectrum is added; on the other hand, the effective radiation from the centre of the line is little if at all increased, for the line becomes conspicuously reversed, the centre being the darkest part.

I have found very great advantage in substituting for the soda flame a sodium vacuum arc in quartz, similar in principle to the familiar quartz mercury arc. The sodium lamp is, of course, considerably more troublesome than the mercury lamp, but of late I have succeeded in making improvements in this respect.

## § 2. *The Sodium Vapour Lamp.*

The present construction of the lamp is shown in fig. 1. (a) is the silica envelope. The electrodes are fitted to it by indiarubber connections, which are sufficiently tight and mechanically better than cement. The cathode (b) is a pool of molten sodium, and connection is made to it by the wire (c), which may be of iron or copper, and fits the silica tube pretty closely. The anode (d) is of tungsten rod, 5 mm. in diameter. This metal, though it gets red hot, seems to stand the action of sodium vapour indefinitely. Iron anodes, on the other hand, after an hour or two of use, fuse and drop off, presumably owing to the formation of an alloy: for the temperature is far below the melting point of iron. To economise tungsten, the actual electrode is ground down to a smaller diameter at one end, and fitted into a hole drilled in an iron rod (e), which is pinched on to it. The iron rod is carried by the brass fitting (f), through which the tube can be exhausted by a Gaede mercury pump, kept continuously in action while the lamp is running.

If the lamp is to last long, the most important point is to run it with only a small current, so as not to heat and reduce the silica of the narrow connecting tube, which is the source of light. The lamp can be run at a current of 5 or 6 ampères without the need for any extraneous heating to raise sodium vapour, except at the start, but so large a current is very hard

on the silica. If it is attempted to reduce the current much by additional resistance, the lamp goes out. After much trouble, it was found that the difficulty could be overcome by gently heating the lower bulb containing melted sodium over a small ring gas burner (*g*), concentric with the lamp. A test made on an empty tube showed that the gas burner alone, as used, kept the inside of the lower bulb at a temperature of about  $180^{\circ}\text{C.}$ , apart from any heating effect of the current. The latter heats the middle and upper part of the lamp more than adequately, but does not raise enough vapour from the sodium cathode without the help of the gas ring. The working current was 2.5 amperes, and did not heat the middle tube of the lamp hot enough to char a piece of paper held against it for a few seconds. With the self-induction of a large electromagnet in the circuit, and on the 200-volt supply, the lamp would run indefinitely without going out. It has been run 24 hours or more, being left unattended all night. The drop of potential over the lamp was very capricious, even after long running at a constant current. It varied from 20 to 50 volts. The sudden movements of the voltmeter seemed to correspond with a wandering of the point of departure of the arc from the sodium surface.

The lamp is started some minutes after lighting the ring burner by means of a small induction coil, one terminal connected to the sodium cathode, the other to a wire twisted round outside the central silica tube. If any difficulty is experienced in starting, it is usually traceable to insufficient exhaustion. I have not been able to start the lamp on a 100-volt supply, although this gives a good margin over the voltage dropped on the lamp while running.

After an aggregate run of 24 hours it is generally advisable to dismount and wash out the lamp, first with alcohol and water, then with weak hydrofluoric acid. This method of removing the brown coating of silicon is better than the use of boiling caustic soda, or than applying the blowpipe.

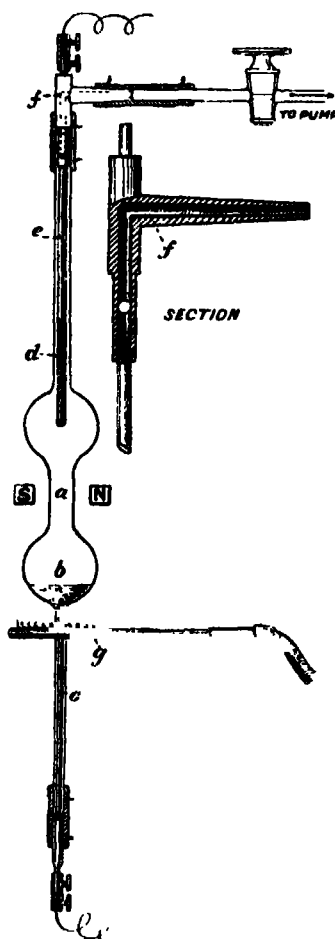


FIG. 1 ( $\frac{1}{3}$  actual size).

§ 3. *Radiation of the Lamp. Minute Structure of the D Lines.*

The D line is by far the strongest in the spectrum, and, in experimenting with it, it is generally unnecessary to use colour screens to cut out the other lines.

If the lamp is used to excite D-line resonance radiation in a bulb containing sodium vapour, most baffling caprice is observed in the intensity of the effect, which will sometimes be extremely brilliant, and at other times will disappear, without obvious change in the conditions.

A Fabry and Perot *étalon* was set up, to examine the structure of the D lines from the lamp, and to test whether the caprice just mentioned could be connected with it. The *étalon* was about 5 mm. thickness, and had to be packed with paper (not an ideal arrangement) to get the distance right for separating the  $D_1$  and  $D_2$  fringes. It was then observed that each of the D lines was reversed, but that the breadth and darkness of the reversal varied with the same caprice that had been observed in the resonance radiation. Sometimes one of the D lines (I did not determine whether  $D_1$  or  $D_2$ ) was much more conspicuously reversed than the other. A weak electromagnet was then arranged to throw the column of discharge against the forward wall of the tube, and squeeze out the reversing layer of cool sodium vapour.\* The reversal was thus made much less conspicuous in the interferometer, though it was never wholly got rid of. Plate 5, No. I, shows the change in the interference rings when the magnet current is reversed. In the top half the discharge is thrown against the front wall of the tube, in the bottom against the back wall. It will be noticed how enormously the reversal is developed by this change.

A strong field tends to concentrate the discharge so much to one side of the tube that the wall becomes unduly heated, with attendant bad effect on the silica. This becomes brown, and may even be locally heated so strongly as to soften and be perforated. In practice the field was not measured, but was increased by moving the magnet or increasing the exciting current, as far as could be done without making the front of the tube hot enough to quickly char paper.

Even in this case the front of the tube deteriorates sooner than the back, which latter is often cool enough for sodium to condense upon it. After a few hours' run it is convenient to turn the tube round on its axis, the india-rubber connection to the pump being long enough to allow of this. Any deposit of sodium then soon clears off, leaving a clear silica wall through which the light can emerge.

\* This is in imitation of the device used by Kerchbaum, 'Electrician,' vol. 73, p. 1074 (1914), with the mercury vapour lamp.

§ 4. *Resonance with D Light.*

With the sodium lamp as described, focussed upon the wall of an exhausted bulb containing sodium vapour, very brilliant resonance is obtained, bright enough to be readily shown in the largest lecture room. This brightness makes possible various experiments which would be very difficult to carry out with the salted flame as a source.

At the lowest temperature and least vapour density where the phenomena are perceptible, the beam, as observed from the side, extends right across the bulb, without losing intensity as it proceeds. With rising temperature, luminosity is not limited to those parts of the bulb traversed by the primary beam, but spreads beyond them. This is due to a tertiary emission, the scattered radiation being itself absorbed and re-emitted. At one stage the whole bulb appears to glow almost uniformly with yellow light.

With further increase of density, the luminosity begins to draw in to the front surface of the bulb, the toll taken from the primary beam being so great that it becomes rapidly impoverished in the effective constituents.

Finally, at temperatures in the neighbourhood of  $300^{\circ}$  C., the emission observed is almost entirely from the front wall of the bulb, and is limited to a skin a fraction of a millimetre in thickness.

Closer examination shows, however, that there is always present as well, a much feebler D emission, which extends with little diminution right across the bulb. Dunoyer\* has observed something of this effect, which he regards as a transition stage between the phenomena of pure volume and pure surface resonance. I have, however, been able to observe it up to the highest temperatures attainable without blackening in glass vessels, and have also observed a volume effect of the same nature in a special iron vessel heated to  $500^{\circ}$  C. As Dunoyer has remarked, it is natural to attribute the superficial resonance to excitation by the core of the D line, and the subsequent luminosity to excitation by less central portions of the line.

When the bulb is observed or photographed from in front, the superficial resonance is overpowering (see Plate, No. III). But, when observed from behind, the superficial resonance is invisible, owing to absorption by the vapour, and the luminous track across the bulb stands out strongly (Plate, No. IV).†

The light emitted along the track, being of slightly different refrangibility from the superficial emission, is not so strongly absorbed, and can emerge through the layer of intervening vapour, and reach the observer's eye. The

\* 'Journal de Physique,' January, 1914.

† The patches of light marking the entrance and exit of the beam in the photograph are due to diffusion by the glass walls.



annexed diagram (fig. 2) will show clearly what is meant by observation from in front and from behind.

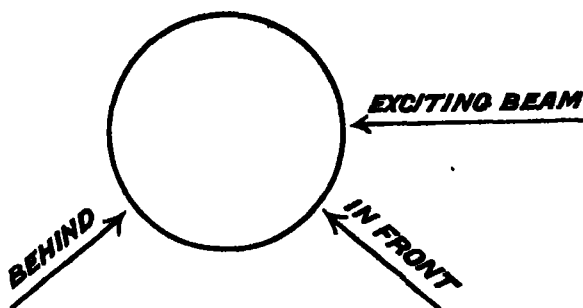


FIG. 2.

The different refrangibilities of the superficial and volume radiation as they emerge from the bulb can be shown by observing it through an independent layer of sodium vapour. A thin steel tube containing sodium was closed at the ends by glass plates cemented on. It could be evacuated and heated electrically to raise sodium vapour. The ends were water-cooled to protect the sealing-wax.

The resonance bulb was photographed from in front through the tube, first cold (Plate, No. IV), then heated to a temperature carefully adjusted by trial to get the right effect (Plate, No. V). It will be noticed that absorption has taken far more toll from the superficial luminosity, which is now so much diminished that it no longer masks the volume effect. No. IV was not given so long an exposure as No. V. If it had been, the brilliant superficial resonance would have blurred the whole picture by over-exposure.

#### § 5. *Breadth of the Resonance D Lines.*

The experiments just described show that the breadth of the resonance line is not a very definite quantity. It increases with the thickness of vapour traversed by the incident beam. It was, however, of interest to examine the superficial resonance under high spectroscopic resolving power. A Lummer plate was used, mounted on a Hilger "wave-length" spectroscope.

The interference pattern is seen in Plate, No. VI. The spectroscope did not separate the two D lines horizontally as widely as might be desired for the present purpose, and this is the more unfortunate in that the thickness of the Lummer plate did not happen to be right for fully separating the  $D_1$  and  $D_2$  fringes vertically. However, they can be seen to be separate vertically in the first few orders, from the bottom of the photograph, which,

of course, corresponds to grazing emergence from the Lummer plate. A wide slit was used, thus  $D_1$  and  $D_2$  are not separated horizontally, except at the right and left edges of the pattern.

The full observable breadth was determined on a measuring machine as 0.192 of the distance between successive orders, and the distance between successive orders can be calculated from data for the Lummer plate supplied by the makers as 0.177 Ångström. This makes the full observable breadth 0.034 Ångström. There is a little uncertainty, owing to the inadequate separation of  $D_1$  and  $D_2$ . It was assumed that the edges of the  $D_1$  and  $D_2$  fringes were just in contact. In any case, however, a measurement of this kind only gives a rough notion of the true breadth of a line as defined by Buisson and Fabry.\*

Assuming a distribution of light of the form  $e^{-kx^2}$ , when  $x$  is the distance along the spectrum from the centre of the line, the half breadth is defined as the distance in which the intensity is reduced to half the maximum. Nearly the whole of the light is contained in something like double this distance. If it is assumed that this corresponds to what was measured on the photograph, the true breadth of the line would be  $0.034/2$  or 0.017 Ångström. The breadth of the line as determined by the Doppler effect, taking the radiator as the sodium atom, and the temperature as  $250^\circ \text{C}$ ., is given by the formula of Buisson and Fabry as 0.0201 Ångström, which agrees as well as can be expected with the value as roughly determined by the Lummer plate. A more satisfactory determination of the breadth of the line could be made with a sliding Fabry and Perot interferometer, but such an instrument was not available. I had, however, the use of a Fabry and Perot étalon of about 3 cm. distance between the plates. A new distance piece was made for it, of such thickness as to bring the  $D_1$  fringes midway between the  $D_2$  fringes. A photograph of the resonance radiation taken with this showed the rings, though they were apparently not very far from the vanishing point.

Taking into account the complications introduced by the selective absorption of the vapour, it is not probable that the resonance lines have the exact intensity distribution which is postulated for definition of the breadth. Thus it seems doubtful whether an attempt to determine the breadth more precisely would have much value.

The general conclusion is that the breadth of the lines is the smallest it could possibly be, if the radiators are monatomic molecules of sodium. The thermal motion of the molecules necessarily gives rise to a broadening of the ideal infinitely narrow line, and this accounts for the whole observed breadth of the line. In some cases, *e.g.*, the condensed discharge in hydrogen, other

\* 'Société Française de Physique,' April 10, 1912.

causes enlarge the line much beyond the limit set by the Doppler effect. But here such causes have no place.

### § 6. *Resonance Radiation at the First Ultra-violet Line.*

In a salted Bunsen flame practically no lines due to sodium except the D line can be observed. With electrical stimulation, for example, with the vacuum lamp described, many other bright lines due to sodium appear, some in the visual spectrum, and some in the ultra-violet. These latter alone fall into the same spectrum series as the D line; apart from the numerical relations of frequency, this is evidenced by the fact that they alone show the same type of Zeeman effect as the D line, and that they alone, like the D line, show as dark absorption lines, even when the vapour is at a moderate temperature and is not electrically stimulated.

My experiments on the ultra-violet lines of this series have been usually limited to the first one, at wave-length 3303. This light is not seriously weakened by passing through thin glass bulbs, and it can be very conveniently freed from D light by passing through cobalt glass, preferably the blue uviol glass made at Jena. Blue light is removed by means of a dilute solution of nitrosodimethyl-aniline. The radiation of the quartz lamp filtered in this way consists exclusively of the first ultra-violet line; the second and higher ones cannot penetrate uviol glass.\*

Since resonance is obtained with the D line, we might expect it at  $\lambda$  3303. My earlier attempts to observe this were unsuccessful, owing, as it now appears, to the small size and bad optical quality of the silica vessels used, which scattered so much light that they masked the effect to be looked for. Owing to the circumstances of the time, the work had to be broken off somewhat hastily. In taking up the subject again, a glass bulb 7.5 cm. in diameter was used, charged with sodium according to Dunoyer's methods, and exhausted as for experiments on the D emission. Thin blown glass is not seriously opaque at  $\lambda$  3303, and the surface is optically better than that of any silica bulbs that I have seen. The bulb was heated to about 250° C., and mounted so that the beam from a limited portion of the lamp, made parallel by a quartz lens, passed diametrically through it. The bulb was

\* These latter lines are feeble unless the lamp is run at heavy currents, in which case its life is short. I have on occasion run the lamp at 30 amperes or more, for a moment or two, heating it thereby till the silica walls collapsed under atmospheric pressure. In this case the relative and actual intensity of the ultra-violet lines is much increased. When the silica is very hot, the brown stain caused by moderate heating in contact with sodium vapour clears off, leaving the walls transparent. It might be feasible to run the lamp for longer periods in this way if an external vacuum jacket were provided to prevent collapse.

photographed laterally, with a quartz lens and blue uviol filter, stopping all D light. The result is reproduced in Plate, No. II. The track of the beam across the bulb is well seen. To verify that this re-emission consisted of  $\lambda$  3303, the bulb was photographed again with a quartz prismatic camera, set up at a distance. Two small monochromatic images of the bulb with the beam stretching across it corresponding to D and  $\lambda$  3303 were obtained. Using an ordinary plate (not colour sensitive),  $\lambda$  3303 was somewhat more intense, but on orthochromatic plates the D image was greatly over-exposed by comparison. The subordinate series lines gave no re-emission. They were represented only by dots corresponding to the point where the beam entered and was partially diffused by the glass wall.

The third line of the principal series would not penetrate even a thin glass bulb. An attempt was made to observe its re-emission, using a quartz sodium bulb and the prismatic camera, but without success, probably from the relatively small intensity of this line in the source. This latter point was not pursued to the utmost. The success now attained in detecting 3303 resonance radiation in contrast to the former failure, is mainly due to the use of a large bulb and a temperature low enough for the radiation to be able to penetrate across the vessel instead of being confined to the neighbourhood of the surface. In this way the resonance radiation is well separated from radiation scattered or reflected by the wall of the vessel. It is true that the volume resonance is likely to be intrinsically faint compared with the superficial, but this is more than compensated by using a photographic plate instead of the fluorescent screen then employed. The photographic method is usually much to be preferred in looking for faint ultra-violet radiation.

### § 7. *Resonance and the Zeeman Effect.*

The resonance radiation so far described, whether at the D line or at  $\lambda$  3303, is an effect apparently quite in harmony with the classical mechanics. Nothing is more natural than that radiations of a certain frequency falling upon a resonator should set the resonator into vibration, and cause it to re-emit the same frequency.

From the same point of view, it is equally natural that a slight disturbance of the tuning should greatly diminish the effect obtained; and so it is found. It is well known from Zeeman's discovery that we can slightly alter the frequency of a spectrum line by placing the radiating or absorbing gas which is responsible for it in a strong magnetic field. It is not convenient to place the vacuum lamp in a strong magnetic field,\* but the experiment

\* The weak magnetic field applied to the lamp, as already described for a different purpose, is not enough to produce an appreciable Zeeman effect.

can be well carried out if a slightly salted Bunsen flame is used. If either this or the sodium bulb is placed in a strong magnetic field the tuning is disturbed, and the resonance radiation much weakened.

§ 8. *Stimulation of D Light by Excitation at the First Ultra-violet Line.*

We now come to another effect, which seems to have no analogy in the behaviour of the vibrating systems dealt with in the classical mechanics. This is the excitation of the lower frequency (D line) by stimulation with the higher one ( $\lambda$  3303). To detect this in experiment, the line 3303 from the sodium lamp must be isolated by ray filters, opaque to visual light, as already described. These filters are set in the wall of a dark room, into which the ultra-violet beam enters, and converges on the walls of a glass or quartz bulb containing sodium vapour. The conditions of this experiment are advantageous, in that there is no "false light" to be feared, and the D line to be looked for is situated in the visually brightest part of the spectrum. Even so, however, it is advisable to carefully rest the eye in the dark for some minutes before beginning observations. With these precautions, the emission of visual light when the ultra-violet beam enters the vapour is well seen, and visual examination with a spectroscope shows the D line only. It is quenched when a piece of thick plate glass is held in the path of the exciting beam.

The general validity of Stokes' law made it seem improbable that D radiation would excite  $\lambda$  3303 in fluorescence. Experiment confirmed this anticipation. Ultra-violet light was cut off from the sodium bulb by putting a piece of plate glass 1.2 cm. thick, and in other tests a quinine cell, between it and the lamp. Photographs through blue uviol glass showed no trace of a beam traversing the glass even with 24 hours' exposure. The outline of the bulb was itself faintly visible, owing to stray light from the burner used to keep it hot.

To return to the emission of D light by stimulation at 3303. The interest of this observation is that it clearly establishes the existence of some mechanical connection between the system which absorbs  $\lambda$  3303 and that which emits the D line.

There are known cases of mechanical connection between two different periods in a vibrating system, for example, Melde's experiment, in which a vibrating string is set in motion by a tuning-fork of half the period, applied so as periodically to alter the tension of the string. The Goldschmidt alternator used in wireless telegraphy is another instance. But in this class of cases the periods are commensurable. I mean that they stand in the same ratio as two *small* whole numbers. The periods of D and  $\lambda$  3303

certainly do not do this. Here we encounter in a simple form the known difficulty of dealing with spectra on accepted mechanical principles.

Although our notions of the mechanism by which spectrum lines are emitted and absorbed are very vague, it seems certain that the quantum relations are concerned. If one quantum of the radiation  $\lambda$  3303 were absorbed, and one quantum of D light emitted, there would remain over one quantum of the radiation  $\lambda$  7519. I have not been able to find this line in the spectrum of the vapour excited by  $\lambda$  3303.\* But, even if the residual energy really goes into this radiation, we could scarcely hope to detect it, taking into account how little sensitive the eye is in this deep red region of the spectrum.

The vapour stimulated by  $\lambda$  3303 emits, as we have seen, both  $\lambda$  3303 and D light. From the quantum point of view, however, it seems improbable that these two radiations are simultaneously emitted by the same molecule, for the absorption of one quantum of  $\lambda$  3303 would allow of emission of the same, but would leave no energy over for the emission of D light.

### § 9. *The Two D Lines Separately Considered.*

In the observations mentioned so far, it has not been necessary to take into account that the sodium lines are double. An interesting field of work was first opened up by the work of Wood and Dunoyer, who found that, if one of the D lines only was used to stimulate the vapour, then that line only was emitted.

Later experiments by Wood and Mohler† have shown that some qualification of this statement is required. It is only valid if the vessel is perfectly free from hydrogen, a condition not easily realised, because of the extraordinary tenacity with which sodium retains hydrogen, even when distilled. It is further necessary that the density of the vapour should be below a certain limit.

As we have seen, stimulation at wave-length 3303 causes emission of the D line. But 3303, like D, is a doublet. This naturally suggested that the corresponding lines of each doublet might be coupled. If so, we might expect to find that stimulation at the more refrangible component of 3303 would lead to emission of D<sub>1</sub> only, without D<sub>2</sub>.

I was able to try this experiment by making use of the fortunate accident that there happens to be a line of the zinc spectrum exactly coincident with the more refrangible number of 3303. Stimulating the sodium vapour by

\* Nor does it ever seem to have been observed from sodium vapour in any case. I could not detect it in the vacuum arc.

† 'Phil. Mag.,' vol. 37, p. 456 (1919).

this source, it was found possible to get a luminescence bright enough for examination with a special spectroscope capable of separating the D lines. The result was to show that both the D lines were emitted, without marked difference of intensity.

At the time this experiment was made, nothing was known of the effect of hydrogen, or excess of sodium vapour, in communicating energy from one D line to the other. It should be repeated in the light of Wood and Mohler's result. For it is now seen to be possible that  $D_1$  alone was directly stimulated by the ultra-violet source,  $D_2$  deriving its energy from  $D_1$ .

The possibility must also be borne in mind that some similar complication may be concerned in the transference of energy between  $\lambda$  3303 and the D lines.

#### § 10. *Polarisation Experiments.*

Dunoyer\* has elaborately examined the polarisation of D resonance. I have repeated some of his experiments in a slightly modified form, preliminary to examining the new ultra-violet resonance at 3303.

For observing weak polarisation, a Savart polariscope is usually employed, but no suitable instrument of this kind was at hand. I found, however, in the laboratory stock a pair of quartz plates, which, when superposed in the right way, gave straight fringes like those of Babinet's compensator, localised in the plates, one of which was wedge-shaped. This combination was set up near the source for examination. Photographs were taken from about 1 metre distance through the quartz plates, and a polarising prism placed over the camera lens. The camera pointed at right angles to the primary beam.

The experiments were made in large glass bulbs. The quartzes were arranged so as to produce fringes perpendicular to the beam stretching across the bulb. With sodium vapour at low density, giving volume resonance only, the fringes were distinct but not strong, and, since they did not appear on the darker background, but only on the bright beam, it seems safe to assume that they indicate genuine though slight polarisation of the scattered light. In experiments of this kind it is necessary to guard carefully against spurious polarisation effects due to the curved glass walls. To minimise these, a bulb of 300 c.c. capacity was used, and observation was through an area of rather less than  $1\frac{1}{2}$  inches diameter.

As the temperature was raised the resonance radiation began to assume the superficial character, but as before, a fainter beam stretched right across the bulb. This was photographed with the polariscope arrangement, and the

\* 'Le Radium,' vol. 2, May, 1912; 'Journal de Physique,' January, 1914.

fringes appeared decidedly less distinct than they had done at lower temperatures.

The loss of distinctness in the fringes with a higher temperature, and the gain with a lower one, was also observed visually, and could be repeated as often as desired.

The newly discovered resonance at  $\lambda$  3303 could be examined in the same way, substituting a blue uviol glass screen for the yellow one, and using ordinary instead of orthochromatic plates. No trace of the fringes could be detected in this case. The polarisation, if any, must be very slight indeed.

The slight degree of polarisation in the case of D light, and its apparent absence with  $\lambda$  3303, is in very remarkable contrast to the nearly complete polarisation observed when ordinary gases scatter white light.\* Unfortunately it is impossible to examine the behaviour of sodium vapour far away from the region of selective absorption and resonance, because of technical difficulties in handling vapour of the necessary density. I have attempted to trace the transition by working as far away from the core of the D lines as possible. The broadened D lines from an oxyhydrogen sodium flame were used as source. The sodium vapour was contained in a cross-shaped iron vessel similar to that used in my studies of the scattering of white light by gases. The light passed through a column of sodium vapour before arriving at the scene of action, and in this way the core of the D lines was removed, leaving only the extreme edges of the lines. Even in this case, as long as any resonance remained observable, it failed to show strong polarisation, so that the transition between ordinary scattering and resonance radiation has not been traced.

The corresponding problem for mercury vapour may prove more tractable. An effort will be made to overcome the difficulties.

#### § 11. *Connection between Line and Band Spectrum.*

The fluorescence of sodium vapour presents puzzling problems even in those simple cases above discussed, when the line spectrum alone is apparently concerned. I do not enter upon the complex phenomena of the band spectrum which Prof. Wood has investigated working with dense sodium vapour. It is desirable, however, to refer to the relation which he has found between the line and the band spectrum in the dense vapour. These are, briefly, that the D lines are excited when stimulation takes in the blue green region giving the channelled absorption spectrum. Also that each line of the principal series is accompanied by a similar channelled absorption spectrum. In the light of these facts it seems doubtful whether any theory

\* 'Roy. Soc. Proc.,' A, vol. 95, p. 155 (1918).



of the line spectrum can be complete which does not take the band spectrum into account. But the complexity of the latter is discouraging. Dunoyer has advocated the view that hydrogen is necessary to the appearance of the fluorescent band spectrum, but this I find difficult to accept.

§ 12. *Summary (including the hitherto unpublished Experimental Work only, without reference to the General Discussion of the whole subject).*

1. The sodium vapour lamp has been improved, and the conditions have been studied for steady running, and for getting the right kind of radiation to excite brilliant resonance with D light.

2. It is found that excitation of sodium vapour by the second line of the principal series leads to the emission of both 3303 and the D line.

On the other hand, as might be anticipated, excitation of the D line leads to the emission of the D line only, with 3303.

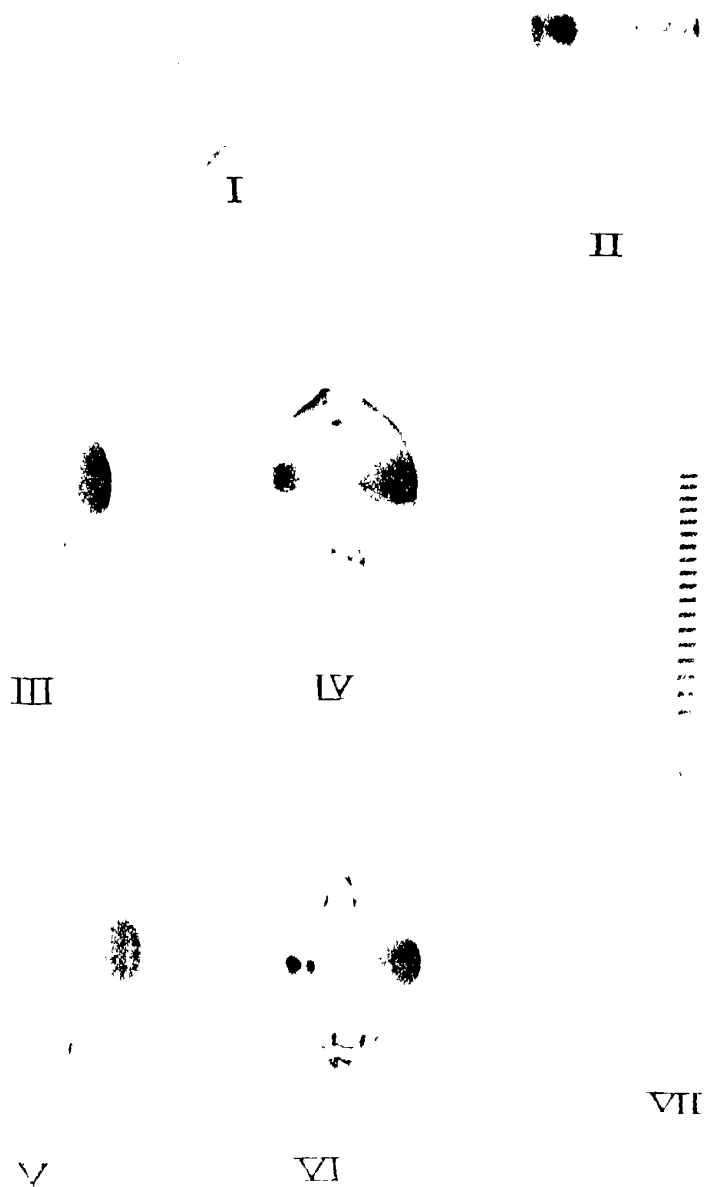
3. When D light falls on sodium vapour of appropriate density, it is known that an intense surface emission occurs from the front layer, and a weak one from succeeding layers. Analysis by absorption in an independent layer of sodium vapour shows that the superficial emission is more absorbable, and therefore nearer the centre of the D lines.

4. The breadth of the D lines in superficial resonance has been estimated by interferometer methods. It is found to correspond with the breadth conditioned by the Doppler effect, on the assumption that the luminous centre is the sodium atom.

5. Polarisation could not be detected in the ultra-violet resonance radiation, though in accordance with previous observers it was readily observed in D resonance.

#### DESCRIPTION OF PLATE.

- I. Interference rings obtained with 5 mm. étalon from sodium lamp. Upper half, with discharge thrown against front silica wall by the magnet. Lower half, magnet reversed, so as to throw discharge against back wall. This greatly develops the reversal of each D line.
  - II. Bulb containing sodium vapour, traversed by the light of sodium lamp. Photographed through blue glass, showing emission of the second line of the principal series.
  - III. Bulb containing sodium vapour, illuminated by a beam from the lamp. Superficial D emission as seen from in front.
  - IV. Ditto. Volume D emission, as seen from back.
  - V. Bulb containing sodium vapour. Photographed without sodium vapour filter.
  - VI. Ditto. Photographed through sodium vapour filter, with longer exposure. Greater relative intensity of the volume effect. The oval patches to the left are false light, due to glass walls.
  - VII. Superficial D resonance, photographed with Lummer interferometer.
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*The Adsorption of Gases at Low and Moderate Concentrations.*  
 Part I.—*Deduction of the Theoretical Adsorption Isostere and Isotherm.* Part II.—*Experimental Verification of the Form of the Theoretical Isosteres and Isotherms.*

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(Communicated by Prof. James Walker, F.R.S. Received July 22, 1919.)

PART I.

In a previous paper\* by the author it was pointed out that for small adsorptions the adsorption isotherm could be represented by the simple relation

$$\alpha = \alpha_0 c$$

where  $\alpha$  is the amount absorbed and  $c$  is the equilibrium concentration outside the adsorbent. The present paper embodies an attempt to evaluate  $\alpha_0$  in the case of gases, and to connect it theoretically with other physical properties. In addition an adsorption formula is developed which applies to gases up to moderate adsorptions, that is up to 30 per cent. of the saturation value.

We will first examine the case of a gas at low concentrations. We will assume that upon the surface of the adsorbent there is a certain volume, determined, presumably, by the range of molecular action, which is occupied by the adsorbate. Then, for the change of energy involved in the adsorption at constant temperature of 1 grm. molecule of the gas by an infinite amount of adsorbent we can write down *three* expressions. The first of these is that obtained from thermodynamical reasoning by the author,† and we write the change of energy‡ as

$$E = V \left\{ T \left( \frac{\partial p}{\partial T} \right)_\alpha - p \right\} = RT^2 \frac{\partial p}{p \partial T} - RT = RT^2 \left( \frac{\partial \log c}{\partial T} \right)_\alpha, \quad (1)$$

where  $pV = RT$  and  $p = cRT$ .

A second and well-known expression may be obtained from the kinetic theory of gases§ and may be written

$$E = RT \log V/V_\alpha$$

\* 'Roy. Soc. Proc. Edin.,' vol. 39, p. 48 (1919).

† *Ibid.*, vol. 38, p. 23 (1918).

‡ Note that  $\alpha$  has been substituted for  $\alpha_0$ , which is the surface excess actually measured and usually differs inappreciably from  $\alpha$ .

§ See, for example, Jeans, 'Dynamical Theory of Gases.'

where  $V_a$  is the molecular volume of the adsorbate. This equation cannot be applied to the case of a liquid and its vapour, which is presumably due to the fact that the expression should really be written as

$$E = RT \log N_a/N$$

where  $N_a$  and  $N$  are the number of impacts per second per unit area by the molecules in the two phases.  $N$  is not proportional to the concentration  $1/V$  unless  $V$  is great. If the adsorption volume is of thickness  $\delta$  comparable with  $\sigma$  the diameter of the molecule of the adsorbate, then the centre of the molecule oscillating in a thin lamina only moves through a distance  $\delta - \sigma$  normal to the surface and not  $\delta$ . Hence if  $S$  is the area of the adsorbent we see that  $N_a$  is proportional to  $\alpha/S(\delta - \sigma)$  and not  $\alpha/S\delta$ , and hence we write our second equation as

$$E = RT \log \frac{V_a}{S(\delta - \sigma)} = RT \log \frac{\alpha}{w \cdot c}, \quad (2)$$

where  $w = S(\delta - \sigma)$ .

The third expression is derived from the ordinary theory of attraction. Suppose the law of attraction of the adsorbent for the gas is given by the expression

$$-\partial E/\partial r = -\mu a^\dagger a_0^\dagger \phi'(r)$$

where  $\mu$  is a universal constant and  $a^\dagger$  and  $a_0^\dagger$  are specific factors of attraction\* for the gas and adsorbent respectively, and  $r$  is the distance measured from some point in the adsorbent to the centre of attraction of the molecule of the gas. Then if  $r_0$  is the mean value of  $r$  for an adsorbed molecule, there being no change in the mean kinetic energy,

$$\begin{aligned} E &= \int_{\infty}^{r_0} \mu a^\dagger a_0^\dagger \phi'(r) dr \\ &= \mu a^\dagger a_0^\dagger \{ \phi(r_0) - \phi(\infty) \} \\ &= \mu a^\dagger a_0^\dagger \phi(r_0). \end{aligned} \quad (3)$$

We may equate any two of the expressions obtained above. Thus from (1) and (2) we have

$$RT^2 \left( \frac{\partial \log c}{\partial T} \right)_a = RT \log \frac{\alpha}{c \cdot w};$$

whence

$$\begin{aligned} \frac{T \partial \log \alpha/c}{\partial T} + \log \frac{\alpha}{c} &= \log w, \\ \frac{\partial T \log \alpha/c}{\partial T} &= \log w, \end{aligned}$$

\* Since the factor is proportional to the square root of the cohesion, we write  $a^\dagger$ . (See Part III of this research.)

and therefore

$$\begin{aligned} T \log \alpha/c &= \text{constant} + \int^T \log w dT \\ &= \text{constant} + T \log w - \int^T \frac{T}{w} \cdot \left( \frac{\partial w}{\partial T} \right)_\alpha dT. \end{aligned} \quad (4)$$

where the constant is some function of  $\alpha$  but is independent of  $T$ . Again from (2) and (3) we have

$$T \log \alpha/c = T \log w + \mu/R \cdot \alpha^\dagger a_0^\dagger \phi(r_0). \quad (5)$$

It is evident from these equations that if we assume  $w$  to be independent of the temperature, then  $\mu \alpha^\dagger a_0^\dagger \phi(r_0)$  is also independent of  $T$ , and we may write

$$T \log \alpha/c = A + BT, \quad (6)$$

where  $A$  and  $B$  are independent of the temperature but are functions of  $\alpha$ . For convenience of calculation it is better to write the above expression in the form

$$\log \alpha/c = B + A/T. \quad (7)$$

This is evidently the equation for the *adsorption isosteres*—lines of constant  $\alpha$ .

Even if  $B$  and  $A$  are not independent of  $T$  if we expand the right-hand side of (7) in powers of  $\alpha$  we get

$$\begin{aligned} \log \alpha/c &= B(0) + \left( \frac{\partial B}{\partial \alpha} \right)_{\alpha=0} \alpha + \\ &\quad + \frac{A(0)}{T} + \frac{1}{T} \cdot \left( \frac{\partial A}{\partial \alpha} \right)_{\alpha=0} \alpha + \\ &= A_0 - A_1 \alpha, \end{aligned} \quad (8)$$

neglecting powers of  $\alpha$  beyond the first for moderate adsorptions. This new expression (8) is evidently the equation for the *adsorption isotherm*—the relation between  $\alpha$  and  $c$  (or  $p$ ) at constant temperature.

It is now necessary to examine to what extent equations (7) and (8) represent the results of observation, and thus to find how far the assumptions made in the simple theory are justified by experiment. For this purpose we will look at some adsorption isosteres and isotherms, and find (i) how far  $A$  and  $B$  are independent of temperature; (ii) to what extent powers of  $\alpha$  beyond the first may be neglected in (8).

## PART II.

### (a) *The Adsorption Isosteres.*

It is as a rule difficult to obtain observations of an adsorption isostere over a very wide stretch of temperature. At high temperatures the adsorption is small save for very great pressures, while at low temperatures the adsorption

is great even for small pressures. The examples here cited have been chosen as covering as wide a stretch of temperature as possible and providing a fair representation of the observations available.

Table I.

Argon (Homfray\*)  $\alpha = 1.67$ .  $\log p/T = 1.520 - 807/T$ .  
 Crit. temp. =  $-117^\circ\text{C}$ .  $\alpha_\infty = 110$ .

$p$ .	$T$	$p$ calc.
cm.		
5	251.0	5.1
10	272.7	10.0
15	286.8	14.6
20	298.0	19.5
25	308.6	25.1
30	316.6	29.9
40	330.8	40.1
50	342.6	50.2
60	352.4	60.1

In Table I,  $T$  has been interpolated by Miss Homfray from observations at different temperatures. The method of interpolation is not that suggested by the equations (7) and (8) above, and hence there is introduced a small unknown error. Wherever possible the author has evaluated by extrapolation† from observations at low temperatures the saturation adsorption which is denoted by  $\alpha_\infty$  in the Tables.

Table II.

Methane (Homfray)  $\alpha = 7.18$ .  $\log p/T = 2.225 - 1050/T$ .  
 Crit. temp.  $-96^\circ\text{C}$ . ( $\alpha_\infty = 98$ ).

$T$ .	$p$ .	$p$ calc.
	cm.	
240	1.7	1.7
255	3.4	3.3
273	6.6	6.6
293	12.8	13.0
319	28.9	27.7
351	61.2	60.8
373	(98.2)	97.0
455	(392)	380

In Table II the values of  $p$  in the second column have been interpolated from observations at constant temperature. The values in brackets are extrapolated. Fig. 1 presents in graphical form the results of other

\* 'Zeita. f. Physikal. Chem.,' vol. 74, p. 129 (1910).

† 'Trans. Farad. Soc.,' vol. 10, p. 167 (1914).

interpolations by the author. The rectilinear form of the  $(1/T, \log p/T)$  curves is obvious.

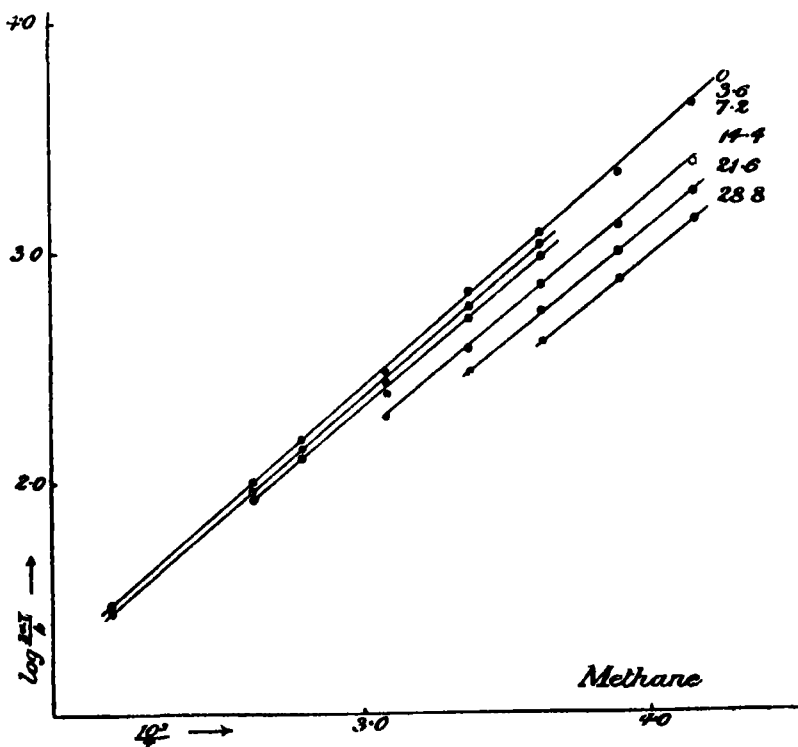


FIG. 1.

Table III.

Carbon dioxide (Chappuis\*)  $\alpha = 282$ .  $\log p/T = 4.269 - 1398/T$ .  
 Crit. temp.  $31^\circ \text{C}$ . ( $\alpha_\infty$  circa 2000).

T.	$p$ (Chappuis).	$p$ .	$p$ calc.
273.0	3.8	3.8	3.8
286.0	7.5	7.0	6.9
290.5	8.7	8.4	8.3
298.7	12.5	11.7	11.6
304.7	15.8	14.7	14.7
308.7	18.7	17.2	17.0
320.0	27.6	25.6	25.4
323.7	31.1	28.8	28.8
329.6	37.8	35.5	35.2
332.8	40.7	38.8	38.4
338.5	48.7	46.8	46.7
343.0	62.8	62.2	62.2
349.1	64.6	68.8	64.1
355.8	77.1	77.1	77.8

\* 'Wied. Ann.,' vol. 12, p. 161 (1881).



In Table III the values headed " $p$  (Chappuis)" have been interpolated by Chappuis on the erroneous assumption that "the increase of adsorption with pressure at any temperature between  $0^{\circ}$  C. and  $83^{\circ}$  C. is proportional to that at  $0^{\circ}$  C." The column headed " $p$ " has been interpolated by the author from Chappuis's observations by plotting on the same sheet the  $(\alpha, \log \alpha T/p)$  points for *all* his observed values at different temperatures and then extrapolating to  $\alpha = 282$ , using the fact that the points for a given temperature lie on a straight line which does not intersect the lines for other temperatures. This extrapolation, though laborious, is very easy. The values of  $\alpha$  in this case refer to 15 c.c. of charcoal—say 27 grm. In all other cases the values are referred to 1 grm. of that adsorbent, the only one here considered.

Table IV.

Ammonia (Richardson\*)  $\alpha = 15$ .  $\log p/T = 3.193 - 1628/T$ .  
 Crit. temp.  $130^{\circ}$  C.  $\alpha_{\infty} = 154$ .

T.	$p$ .	$p$ calc.
	cm.	
273	0.6	0.5
283	0.9	0.8
293	1.3	1.3
303	2.0	2.0
313	3.0	3.1
323	5.5	5.5
343	9.6	9.6
358	16.1	15.8
373	25.6	25.1
388	37.9	36.5
408	56.5	57.3
418	83.4	83.0
433	116	117
448	158	162
473	268	267

The observations on ammonia considered in Table IV are interesting inasmuch as most have been made at temperatures *below* the critical point. The deviations at the lowest temperatures, though small, are apparently systematic and are emphasised in the isosteres for greater values of  $\alpha$ , which are presented in graphical form in fig. 2.

The special case of the isostere of zero adsorption is considered in Part III where many examples are discussed in connection with the theoretical aspect of the constants  $A$  and  $B$  of the formula.

\* 'Jour. Amer. Chem. Soc.,' vol. 39, p. 1828 (1917).

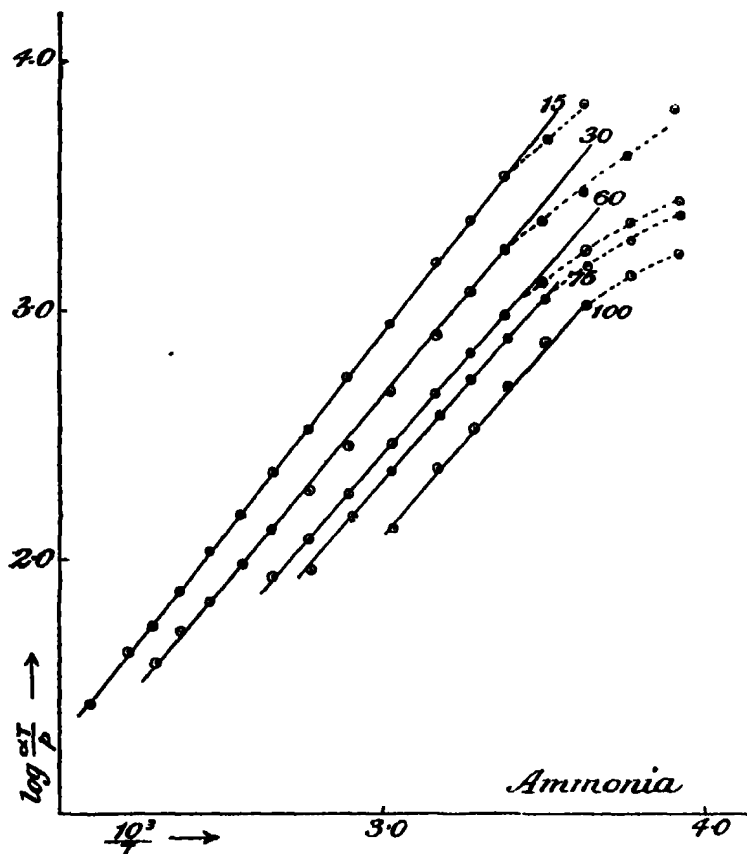


FIG. 2.

(b) *The Adsorption Isotherms.*

As examples of the applicability of the formula (8) the cases below are selected from a mass of data and calculations. For comparison there are also given the values calculated from the best values of the constants in the well-known "exponential" formula

$$\alpha = \alpha_0' c^{1/n}$$

in the form

$$\log \alpha = \log \alpha_0' + 1/n \log c.$$

Table V.

Nitrogen at 0° C. (Titoff\*)  $\log \alpha/p = 1.415 - 0.0143 \alpha$  (I).  
 Crit. temp.  $-146^\circ$  C.  $\alpha_\infty = 96$ .  $\log \alpha = 1.424 + 0.927 \log p$  (II).

$p$ .	$\alpha$ Obs.	$\alpha$ Calc. (I).	$\alpha$ Calc. (II).
cm.	c.c.		
0.43	0.111	0.111	0.123
1.21	0.298	0.312	0.318
3.98	0.987	0.990	0.988
12.98	3.04	3.06	2.87
22.94	5.08	5.06	4.81
34.01	7.05	7.02	7.02
56.28	10.31	10.37	11.12
77.48	13.05	13.09	14.80

Table VI.

Methane at 0° C. (Homfray, *loc. cit.*)  $\log \alpha/p = 0.166 - 0.0165 \alpha$  (I).  
 Crit. temp.  $-95^\circ$  C. ( $\alpha_\infty = 98$ ).  $\log \alpha = 0.497 + 0.545 \log p$  (II).

$p$ .	$\alpha$ Obs.	$\alpha$ Calc. (I).	$\alpha$ Calc. (II).
cm.	c.c.		
6.7	7.4	7.4	9.1
13.4	12.3	12.3	12.8
19.1	15.9	15.5	15.7
27.4	19.1	19.3	19.0
35.8	22.3	22.4	22.0
45.1	25.3	25.2	25.0
57.8	28.4	28.6	28.8
70.2	31.3	31.3	32.0

Table VII.

Carbon monoxide at  $-82^\circ$  C. (Homfray).  $\log \alpha/p = 1.132 - 0.0219 \alpha$  (I).  
 Crit. temp.  $-41^\circ$  C. ( $\alpha_\infty = 94$ ).  $\log \alpha = 1.062 + 0.400 \log p$  (II).

$p$ .	$\alpha$ Obs.	$\alpha$ Calc. (I).	$\alpha$ Calc. (II).
cm.			
0.6	6.2	6.2	9.4
3.0	17.1	17.1	17.9
4.0	19.4	19.9	20.1
7.2	25.7	26.1	25.4
7.5	26.2	26.6	25.8
11.7	31.7	31.3	30.8
14.8	34.7	34.7	33.9
18.7	37.6	37.6	37.2
28.8	43.3	43.4	44.3
42.2	49.3	48.8	51.5

\* 'Zeits. f. Physikal. Chem.,' vol. 74, p. 641 (1910).

The close agreement of the theoretical formula with experiment is shown by the very numerous observations of Chappuis\* contained in Table VIII. These are probably the most accurate existing data at any one temperature. They illustrate also the systematic increasing deviation between the calculated and observed values when the adsorption becomes great. The divergence otherwise appears to be within the limits of error of observation of the pressure and is nowhere large, save initially, and here an error of only 0.023 cm. would cover the deviation, since the calculated value of  $p$  for  $\alpha = 10.45$  is 0.090.

Table VIII.

Carbon dioxide at 0° (Chappuis).  
Crit. temp. 31° C. ( $\alpha_{\infty}$  circa 2000).

$$\log \alpha/p = 2.0727 - 0.000720 \alpha.$$

$p$ .	$\alpha$ Obs.	$\alpha$ Calc.	Per cent. div.
cm.	c c		
0.113	10.45	13.0	+ 24.0
0.223	23.18	25.2	+ 9.0
0.305	34.0	33.9	- 0.3
0.470	52.7	50.9	- 3.4
0.580	61.5	61.7	+ 0.3
0.670	71.9	70.3	- 2.2
0.780	81.8	80.2	- 2.0
0.905	91.2	91.6	+ 0.4
0.986	100.8	98.6	- 2.0
1.100	110.1	108.2	- 1.7
1.240	119.9	119.8	- 0.1
1.352	120.5	128.6	- 0.7
1.495	139.6	139.7	+ 0.1
1.625	140.8	149.4	+ 0.1
1.762	158.9	159.3	+ 0.3
1.882	168.4	167.0	- 0.8
2.012	178.2	176.8	- 0.8
2.170	188.1	187.4	- 0.4
2.312	198.1	196.5	- 0.8
2.494	208.4	207.9	- 0.2
2.641	218.8	217.0	- 0.6
2.822	228.3	227.8	- 0.2
2.998	238.2	238.0	- 0.1
3.175	248.1	247.9	- 0.1
3.392	258.3	259.8	+ 0.6
3.548	268.2	268.1	- 0.0
3.755	278.5	278.6	+ 0.0
3.975	289.6	289.8	+ 0.1
4.194	300.5	300.5	± 0.0
4.427	311.1	311.4	+ 0.1
4.693	324.4	323.5	- 0.3
5.078	341.2	340.2	- 0.3
5.463	357.8	356.7	- 0.3
5.984	377.5	377.5	± 0.0
6.413	393.2	393.8	+ 0.2
6.567	398.8	399.5	+ 0.2
7.010	414.2	415.4	+ 0.3
7.712	438.2	439.3	+ 0.3

\* *Loc cit.*

Table VIII—*continued.*

<i>p.</i>	$\alpha$ Obs.	$\alpha$ Calc.	Per cent. div.
cm.			
8.548	404.6	405.9	+ 0.3
9.437	401.8	402.3	+ 0.1
10.41	519.4	519.2	- 0.0
11.61	547.6	547.8	+ 0.0
12.63	575.8	574.9	- 0.2
13.80	602.8	601.5	- 0.2
15.14	630.8	629.8	- 0.2
16.58	659.2	658.2	- 0.2
18.05	686.4	685.8	- 0.2
19.67	714.2	713.2	- 0.1
21.57	744.0	743.3	- 0.1
23.67	774.5	774.8	+ 0.0
25.81	804.2	804.6	+ 0.0
28.17	833.7	835.0	+ 0.2
30.84	863.4	867.0	+ 0.4
33.50	892.8	896.8	+ 0.4
36.47	921.6	927.8	+ 0.7
39.68	950.6	958.8	+ 0.9
43.05	978.2	989.3	+ 1.1
46.40	1006	1019	+ 1.3
50.86	1038	1049	+ 1.6
54.81	1069	1077	+ 1.7
59.20	1097	1112	+ 2.3
64.64	1114	1147	+ 3.0
70.84	1140	1182	+ 3.7
76.84	1166	1216	+ 4.3

In view of the use that the author has made of the equation (8) in extrapolating to the value of  $\log \alpha/c$  at zero concentration, discussed at length in Part III, it is of interest to examine the complete ( $\alpha$ ,  $\log \alpha/c$ ) curve. This is presented in fig. 3, which is based upon the author's observations\* on sulphur dioxide at  $-10^\circ \text{C}$ ., that is,  $165^\circ \text{C}$ . below its critical point. It will be seen that there are three portions—A to B, B to C, C to D—any one of which might be approximately represented by a straight line. In the case of gases *below* their critical temperature the portion AB becomes very steep, and extrapolation to A is difficult. This is shown by ammonia in the case of the observations of Titoff and of Richardson even *above* the critical temperature, and hence in these cases the equation (8) cannot be used for extrapolation. In the other cases examined, mainly gases *above* their critical temperature, the portion A to C is very nearly rectilinear, and extrapolation is consequently justifiable for observations up to 30 per cent. of the saturation adsorption, and is exemplified in the case of ethylene in fig. 4, in Part III.

\* 'Proc. Roy. Soc. Edin.,' vol. 37, p. 161 (1917).

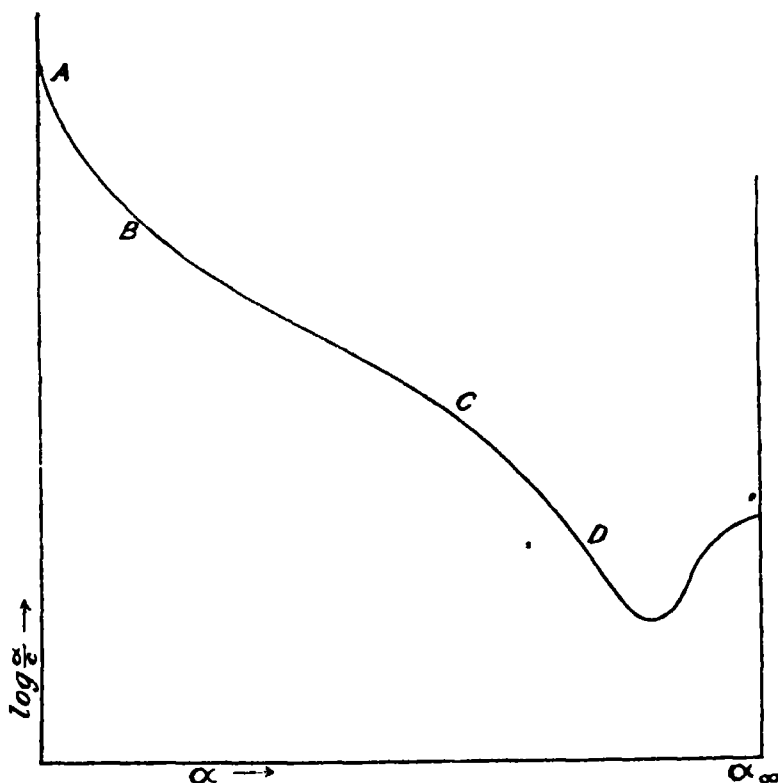


FIG. 3.

*Summary of Parts I and II.*

1. The theoretical form of the adsorption isostere is deduced and found to be

$$\log a/c = B + A/T$$

where B and A are functions of  $\alpha$  only.

2. The agreement with observation for gases above or near the critical temperature is satisfactory.

3. The theoretical form of the adsorption isotherm is deduced and found to be

$$\log a/c = A_0 - A_1\alpha$$

where  $A_0$  and  $A_1$  are functions of the temperature only.

4. The agreement with observation up to moderate adsorptions of gases above their critical temperature is satisfactory.

The author wishes to thank Prof. James Walker, F.R.S., for his valuable assistance in the presentation of this paper.

*The Adsorption of Gases at Low and Moderate Concentrations.*  
 Part III.—*Experimental Verification of the Constants in the*  
*Theoretical Adsorption Isostere.*

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 Edinburgh.

(Communicated by Prof. JAMES WALKER, F.R.S. Received July 22, 1919.)

PART III.

Having established the form of the theoretical isosteres and isotherms, it is now possible and desirable to find how far the constants of the deduced expressions fall in with their theoretical values. We will in the present paper confine ourselves to a consideration of the constants A and B of the zero isostere. These are given by equation (7) in

$$\log \left( \frac{\alpha}{c} \right)_{\alpha=0} = B(0) + \frac{A(0)}{T}$$

and they are also given by  $A_0$  in equation (8),

$$\log \alpha/c = A_0 - A_1\alpha$$

since

$$A_0 = B(0) + \frac{A(0)}{T}.$$

(a) *Miss Homfray's Observations.\**

There exists only one set of observations sufficiently extensive to be suitable for our present purpose.

Miss Homfray's observations embrace the adsorption by cocoanut charcoal of helium, argon, nitrogen, carbon monoxide, methane, carbon dioxide, and ethylene, and it has been found possible to evaluate  $A_0$  for all these gases at various temperatures. Accurate extrapolation from the observations was sometimes difficult in the case of the first two gases which show many irregularities in the data, but was relatively easy with the others. Fig. 4 represents graphically the extrapolation in the case of ethylene, and illustrates the power and scope of the method adopted. It is, of course, obvious that the further away from  $\alpha = 0$  the observations lie, the less reliable is the extrapolation, and the assumption has been made that there is no change in curvature in the graphs near  $\alpha = 0$ , since such is not found in the case of those curves with values available near  $\alpha = 0$ . In extrapolating, repeated use was made of the fact that the gradient of the  $(\alpha, \log \alpha/c)$  curves varies

\* 'Zeit. f. Physikal. Chem.,' vol. 74, p. 129 (1910).

continuously with the temperature. This was helpful in the case of observations at low temperatures when few points were available near  $\alpha = 0$ , and

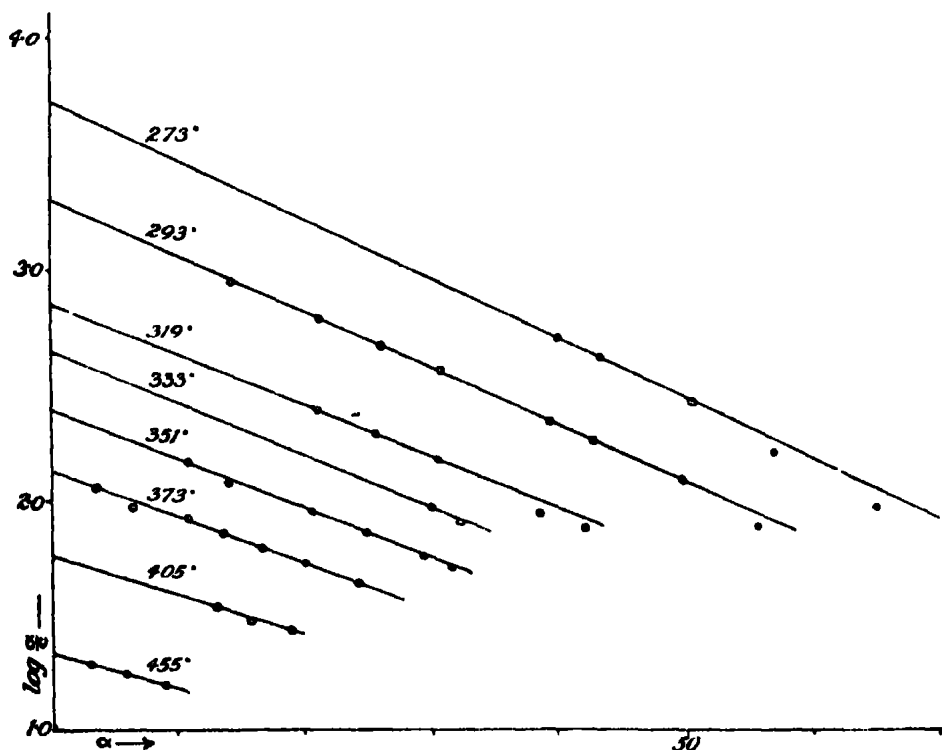


FIG. 4.

was also used at high temperatures where perhaps only one observation was recorded. The error in extrapolating here would be small, since the point was always near  $\alpha = 0$ . But in a few cases the readings are so discordant that only a mean value can be given with a big probable error. This was particularly the case with argon.

The values of  $A_0$  thus obtained have been plotted against the reciprocal of the absolute temperature in order to test (7), and the curves are shown in fig. 5. It will at once be seen that the graphs closely approximate to straight lines, that is,  $A$  and  $B$  are appreciably independent of the temperature over the range studied. This is more closely examined in the Tables following, where a comparison is made of the observed and calculated values of  $\log a/c$  for different temperatures. As regards the constants  $A$  and  $B$ , the difference between  $\log a/c$  calculated and observed is the error in  $B$  if  $A$  is regarded as known, and the last column gives the variation in the



constancy of  $A$  when  $B$  is regarded as known. The real test of the formula, however, is the percentage error in the calculated value of  $a/c$ .

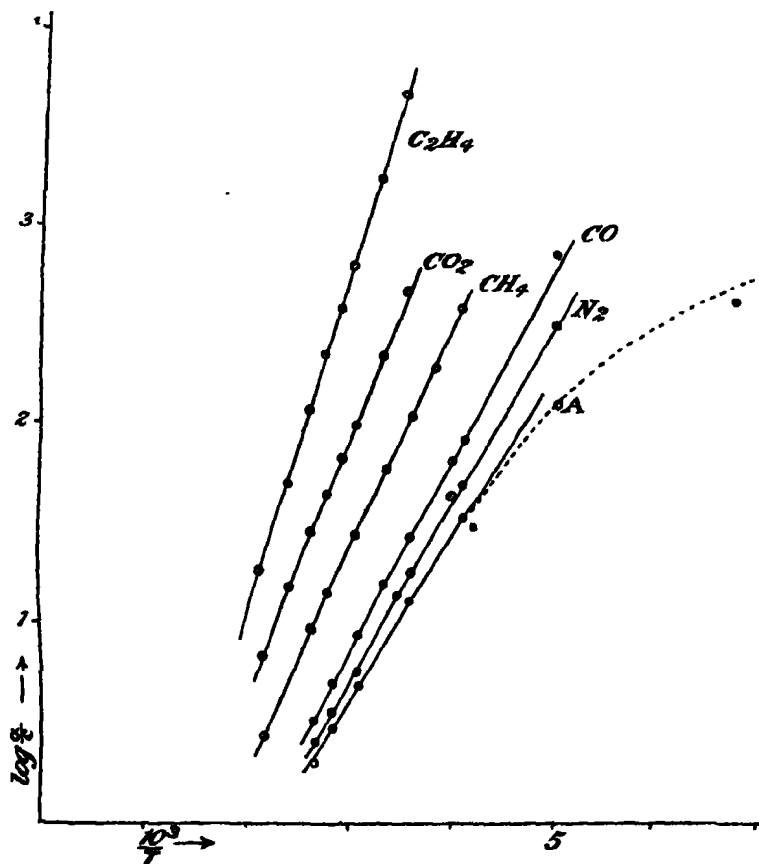


FIG. 5.

Table IX.

Ethylene.  $T_c = 283$ . $B = 3.676$ .  $A = 1631$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
273	3.669	3.651	-0.008	-1.9	1633
293	3.227	3.243	+0.016	+3.8	1627
310	2.792	2.789	-0.003	-0.7	1632
333	2.572	2.574	+0.002	+0.5	1630
351	2.330	2.322	-0.008	-1.9	1634
373	2.057	2.049	-0.008	-1.9	1634
405	1.700	1.703	+0.003	+0.7	1639
455	1.261	1.261	$\pm 0.000$	$\pm 0.0$	1631

Table X.

Carbon dioxide.  $T_c = 304$ . $B = 2.085$ .  $A = 1245$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
273	2.671	2.666	-0.015	-3.5	1249
298	2.843	2.844	+0.001	+0.2	1245
319	1.987	1.998	+0.011	+2.6	1241
333	1.822	1.834	+0.012	+2.8	1241
351	1.646	1.641	-0.005	-1.2	1246
378	1.445	1.438	-0.012	-2.8	1249
405	1.174	1.169	-0.005	-1.2	1247
455	0.828	0.831	+0.003	+0.7	1244

Table XI.

Methane.  $T_c = 178$ . $B = 2.068$ .  $A = 1081$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
240	2.583	2.572	-0.011	-2.6	1084
255	2.295	2.307	+0.012	+2.8	1078
273	2.088	2.028	-0.010	-2.3	1084
298	1.774	1.757	-0.017	-4.0	1086
319	1.440	1.456	+0.016	+3.8	1075
351	1.161	1.147	-0.004	-0.9	1082
378	0.967	0.966	-0.001	-0.2	1081
455	0.489	0.444	+0.005	+1.2	1079

Table XII.

Carbon monoxide.  $T_c = 132$ . $B = 2.014$ .  $A = 933$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
194.7	2.865	2.806	-0.059	-14.6	944
239.4	1.908	1.911	+0.003	+0.7	933
244.5	1.815	1.830	+0.015	+3.5	939
273	1.427	1.431	+0.004	+0.9	932
298	1.196	1.198	+0.002	+0.5	932
319.2	0.935	0.935	$\pm 0.000$	$\pm 0.0$	933
351	0.697	0.672	-0.025	-5.9	941
378	0.515	0.516	+0.001	+0.2	933

Table XIII.

Nitrogen.  $T_c = 127$ . $B = 2.110$ .  $A = 856$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
194.7	2.500	2.506	-0.003	-0.7	857
239.4	1.688	1.686	+0.003	+0.7	855
244.5	1.641	1.611	-0.030	-7.2	863
273	1.249	1.245	-0.004	-0.9	857
282.8	1.140	1.143	+0.003	+0.7	855
306.5	0.690	0.904	+0.005	+1.2	855
320	0.740	0.785	+0.036	+8.6	844
351.2	0.557	0.544	-0.009	-2.1	859
373	0.409	0.405	-0.004	-0.9	857

Table XIV.

Argon.  $T_c = 156$ . $B = 2.11$ .  $A = 822$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	A calc.
145	(2.6 P)	3.78	(651)
195	2.06-2.12	2.33	770-782
236	1.50-1.55	1.59	800-811
273	1.124	1.12	823
321	0.67-0.71	0.67	822-835
351	0.43-0.53	0.45	815-850
373	0.23-0.31	0.31	791-821

The values of A and B for argon given in Table XIV were not deduced directly from the graph, owing to the difficulty in evaluating  $A_0$ . They were deduced by extrapolation from the values for A and B obtained from the isosteres for finite adsorptions tabulated by Miss Homfray. (See, for example, Table I, Part II.)

From the Tables it will be seen that A and B are appreciably constant over a range of some 200 degrees Centigrade, and this indicates from the theoretical discussion that in the region of temperature in question  $r_0$  and  $w$  are appreciably constant, that is, the range of cohesive forces is appreciably constant. The values for argon would, however, indicate that at lower temperatures  $w$  increases. This must be interpreted to mean that the molecule is less closely held to the attracting surface at low temperatures. The curves are, therefore, only *approximately* straight lines, and we are at present unable to predict whether they will remain so at higher temperatures.

Let us now examine a little more closely the physical meaning of the constants A and B. From the theoretical equations of Part I

$$A = \mu/R \cdot a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi(r_0).$$

For the same adsorbing surface  $A/a^{\frac{1}{2}}$  is proportional to  $\phi(r_0)$ , and if the mean distance  $r_0$  is closely the same for different substances, then  $\phi(r_0)$  is closely the same.  $a^{\frac{1}{2}}$  represents the specific attraction of the adsorbed substance, while the cohesion represents the attraction of the substance for itself and should therefore be proportional to  $a^{\frac{1}{2}} \times a^{\frac{1}{2}}$  or  $a$ . We may take the  $a$  of Van der Waal's equation

$$(p + a/v^2)(v - b) = RT$$

to give us a measure of the cohesion factor of different substances. In the Table following this value of  $a$  has been used and is the mean of the values calculated from observations and given in Landolt-Börnstein's tables, save in the case of helium, where the data of Onnes\* have been employed. The last

Table XV.

Substance.	$a$ .	$a^{\frac{1}{2}}$	$A$	$A/a^{\frac{1}{2}}$ .
He	0.000060	0.0083	134	$1.61 \times 10^4$
A	0.00259	0.0508	822	1.62
N <sub>2</sub>	268	518	856	1.65
CO	280	529	933	1.76
CH <sub>4</sub>	367	606	1081	1.78
CO <sub>2</sub>	701	837	1245	1.49
C <sub>2</sub> H <sub>4</sub>	886	941	1631	1.73

column indicates that  $\phi(r_0)$  is indeed appreciably constant for different gases, and hence we see that we have here a new method of placing the values of the internal cohesion of gases.

We get further information as to  $r_0$  and  $\delta$ , the mean effective range of molecular action from B, since

$$B = \log w, \quad \text{and} \quad w = S(\delta - \sigma).$$

If  $r_0$  (and therefore  $\delta$ ) is the same for all the molecules considered, on graphing  $w$  against  $\sigma$  we should obtain a straight line, the gradient of which is the area  $S$  of 1 gram. of the adsorbent, while the intercept on the  $\sigma$  axis is  $\delta$ , and the intercept on the  $w$  axis is  $S\delta$ , the initial volume of the surface film.

Since Van der Waal's " $a$ " has been employed for estimating the cohesion,  $\sigma$  has been recalculated from his " $b$ " by means of the relation

$$\sigma = (3b/2\pi N)^{\frac{1}{3}},$$

and the data are presented in Table XVI. The value of  $\sigma$ , calculated from the viscosity relation by Sutherland, is also given for comparison, and is denoted by  $\sigma'$ . The  $(\sigma, w)$  curve is shown in fig. 6, and the line is the most

\* 'Proc. Acad. Sci. Amsterdam,' vol. 14, p. 678.

Table XVI

Gas	$b$	$\sigma$	$\sigma'$	$B$	$w$	$\delta$	$\delta'$
A	0.00137	$2.88 \times 10^{-8}$	$2.66 \times 10^{-8}$	2.11	0.0129	$3.87 \times 10^{-8}$	$3.93 \times 10^{-8}$
N <sub>2</sub>	171	3.10	2.95	2.110	129	4.09	4.12
CO	170	3.09	2.74	2.014	108	3.88	3.68
CH <sub>4</sub>	160	3.03	—	2.068	117	3.93	—
CO <sub>2</sub>	191	3.21	2.90	2.085	122	4.15	4.01
C <sub>2</sub> H <sub>4</sub>	253	3.53	3.31	3.676	047	3.87	3.74

likely through the points shown. It will be seen that in the case of nitrogen and carbon dioxide the points lay well off the line. In the case of carbon dioxide this corresponds to the low value of  $A/a^{\frac{1}{2}}$  in Table XV, making  $\phi(r_0)$  small, and hence  $r_0$  and  $\delta$  large. The gradient of the line shown is

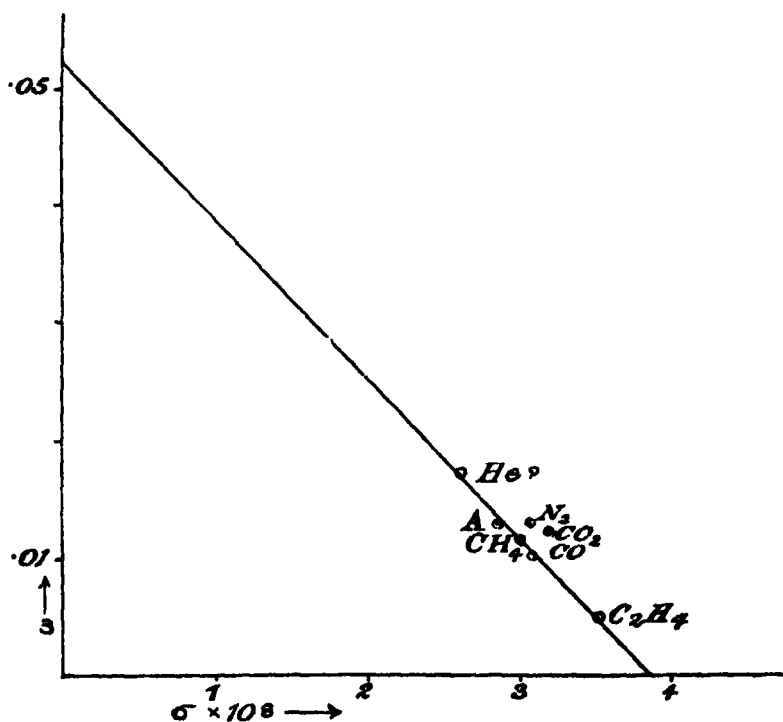


FIG. 6.

$1.31 \times 10^6$ , and hence we conclude that the area of 1 gm. of the adsorbent is  $1.31 \times 10^6$  sq. cm. Assuming the area is  $1.3 \times 10^6$  sq. cm., the author has calculated  $\delta$  in Table XVI for the various gases from the relation

$$w = S(\delta - \sigma).$$

If we use  $\sigma'$  instead of  $\sigma$ , the likeliest line gives  $S = 1.07 \times 10^6$  sq. cm., and taking this value  $\delta'$  has been calculated. It should be noted that if  $r_0$ , and therefore  $\delta$ , varies from substance to substance, the  $(\sigma, w)$  points will not lie on a straight line, but straight lines whose gradient is the value of the area  $S$  through the points in question will intercept on the  $\sigma$  axis  $\delta$  values corresponding to the various  $r_0$  values.

Our calculations, then, lead us to the conclusion that the area of 1 gm. of the charcoal used by Miss Homfray was initially  $1.3 \times 10^6$  sq. cm., and the thickness of the initial adsorption film was approximately  $4.0 \times 10^{-8}$  cm., giving the volume of this film as 0.052 c.c. If we assume the charcoal (density 1.67) to be made up of  $n$  thin laminae, the thickness  $t$  is given by the equations

$$nS't = 0.6,$$

$$2nS' = 1.3 \times 10^6,$$

whence 
$$t = \frac{1.2}{1.3} \times 10^{-6} = 90 \times 10^{-8} \text{ cm.}$$

On the other hand, if we assume the charcoal made up of  $n$  spheres of radius  $r$ , we have

$$\frac{4}{3} n\pi r^3 = 0.6,$$

$$4n\pi r^2 = 1.3 \times 10^6,$$

whence 
$$r = \frac{1.8 \times 10^{-6}}{1.3} = 140 \times 10^{-8} \text{ cm.}$$

On both assumptions we see that the thickness of the adsorbent is great compared with the adsorption layer, and hence we are justified in assuming that the adsorption film may be represented as of volume  $S \times \delta$ .

Reverting now to the points which are off the line the explanation for carbon dioxide has already been given in the low value of  $\phi(r_0)$ —the reason for this itself is not obvious. In the case of nitrogen the value of  $\phi(r_0)$  is not so low as to be attributed to the uncertainty of the  $a$  values as accurate measures of the cohesion. It is therefore of interest to use the value of  $w$  corresponding to  $\sigma$  from the line in fig. 6, and see if this gives us a constant value of  $A$  in the equation

$$\log a/c = \log w + A/T.$$

The values of  $w$  and  $A$ , already given, were selected as the best for reproducing the observed values. The two values of  $A$  are compared in Table XVII below.

It will be noted that the constancy of  $A$  (II) is not quite so good as that of  $A$  (I), but it is possible that more accurate observations might have led to  $A$  (II), and therefore to a more likely value of  $w$  for the  $(\sigma, w)$  curve.

Table XVII.

$$A = T (\log \alpha/c - \bar{2}.110) \quad (I).$$

$$A = 856 \quad (I).$$

$$A = T (\log \alpha/c - \bar{2}.079) \quad (II).$$

$$A = 865 \quad (II).$$

T.	A (I)	A (II).	$\Delta$ (I)	$\Delta$ (II).
194.7	857	863	1	- 2
239.4	855	863	- 1	- 2
244.5	863	871	7	6
273	857	866	1	- 1
282.3	855	864	- 1	- 1
306.5	855	864	- 1	- 1
320	844	854	-12	-11
351.2	859	871	3	6
378	857	869	1	4
			$\Sigma \Delta^2 = 208$	$\Sigma \Delta^2 = 220$

The observations on the adsorption of helium merit a brief discussion. It has already been remarked (in a footnote to Part I) that what is observed is not  $\alpha$  but  $a$ , the excess of the surface concentration over the concentration in the gaseous phase. Assuming no change in the volume of the adsorbent we have, in fact,

$$a = \alpha \left(1 - \frac{V_s}{V}\right)$$

whence

$$a/c = \alpha/c - \alpha V_s/cV = \alpha/c - S\delta$$

and therefore

$$\alpha/c = a/c + S\delta.$$

For small values of  $a/c$  we cannot neglect  $S\delta$ . These small values only occur in the observations at higher temperatures with argon, nitrogen, and methane, and the correction does not seriously affect the results. With helium, however, the case is different. Of the observations on this gas, unfortunately only those at  $83^\circ$  A are sufficiently extensive to be employed. Here we have  $\log \alpha/c = \bar{1}.81$  or  $\alpha/c = 0.65$ . If we employ the data of Onnes (*loc. cit.*),  $T_c = 5.25$ ,  $p_c = 2.26$  atmospheres, whence  $a = 0.000069$ ,  $b = 0.00106$  leading to  $a^b = 0.0083$ , and  $\sigma = 2.65 \times 10^{-8}$ . We may use these values to solve for  $A/a^b$  in

$$\log(a/c + S\delta) = \log S(\delta - \sigma) + A/T$$

where  $S\delta = 0.052$ ,  $S\sigma = 0.035$ , leading to

$$\log(0.65 + 0.05) = \log 0.017 + A/83.$$

$$A = 83 \times (\log 0.70 - \log 0.017),$$

$$= 83 \times 1.61,$$

$$= 134.$$

Hence 
$$\frac{A}{a^{\frac{1}{2}}} = \frac{134}{0.0083} = 1.61 \times 10^4.$$

which is in good agreement with the values obtained for other gases. (The  $\sigma'$  values lead to  $1.52 \times 10^4$ .)

It is evident that if the theory holds for higher temperatures the *observed* adsorption of a gas will vanish, when

$$\log S\delta = \log S(\delta - \sigma) + A/T.$$

Thus, in the case of helium there should be no observable adsorption (or, rather, *very small negative* adsorption) after the point given by

$$\log 0.052 = \log 0.017 + 134/T,$$

or

$$T = 134/0.49 = 270,$$

and in fact Miss Homfray records zero adsorption at 287°A and 290°A.

Miss Homfray elsewhere mentions that at 83°A, 3 gm. of charcoal adsorbed 330 c.c. of argon at its saturation vapour pressure. Assuming the adsorbed film to have a density the same as liquid argon, we see that the volume of the film per gramme charcoal was

$$\frac{110 \times 40}{22400 \times 1.4} \quad \text{or} \quad 0.14 \text{ c.c.}$$

This is less than thrice  $S\delta$  or five times  $S\sigma$ , so we see that the transition layer between adsorbent and saturated vapour is not more than 5 molecules thick. This is what we might expect from the smallness of the value of  $\delta$ , the effective range of the molecular forces. The evidence here presented as to the value of  $\delta$  must be regarded as affording support to the views advocated amongst others by Langmuir as to the smallness of the range of molecular attraction.

#### (b) *Titoff's Observations.*

The only other set of observations which are at all extensive is due to Titoff,\* and includes data for hydrogen, nitrogen, carbon dioxide, and ammonia. Only the observations on hydrogen, nitrogen, and carbon dioxide may be used for extrapolation by means of equation (8), and the results for the two latter gases are given below in Tables XVIII and XIX :—

\* 'Zeits. f. Physikal. Chem.,' vol. 74, p. 641 (1910).



Table XVIII.

Nitrogen.  $T_c = 127$ . $B = 2.515$ .  $A = 759$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A.
194	(2.20)	2.43	+0.23	+70	714
278	1.296	1.295	-0.001	-0.2	759
303	1.019	1.020	+0.001	+0.2	759
353	0.666	0.665	-0.001	-0.2	759
424.5	0.290	0.304	+0.014	+3.3	753

Table XIX.

Carbon dioxide.  $T_c = 304$ . $B = 3.825$ .  $A = 1396$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A.
196.5	(5.04)	4.99	-0.11	-29	1419
278	2.917	2.938	+0.021	+5.0	1390
303	2.430	2.433	+0.003	+0.7	1395
353	1.788	1.780	-0.008	-0.7	1397
424.5	1.113	1.114	+0.001	+0.2	1396

Values of  $A_0$  cannot be directly determined from the isotherms for ammonia for the reason mentioned in Part II—the  $(\alpha, \log a/c)$  curves are not straight lines. Values of  $A$  and  $B$  may, however, be determined from the isosteres for finite adsorptions as was done with argon. We have the following Table:—

Table XX.

$\alpha$ .	60	40	30	20	10	0
A	1360	1405	1428	1450	1487	1540
B	2.840	2.268	2.230	2.196	2.172	2.160

The zero values are extrapolated assuming no change in curvature of the  $(\alpha, A)$  and  $(\alpha, B)$  curves. But the change in curvature of the  $(\alpha, \log a/c)$  curves occurs just below  $\alpha = 10$ , and the assumption is scarcely justifiable, as the values suggested by this consideration are much lower for  $A$  and much higher for  $B$ . Nevertheless, the values given in the Table may be employed as representing a possible  $(\phi(r_0), \delta)$  configuration of the system, even if it is not the one actually occurring with ammonia at zero concentration.

The observations with hydrogen are at three temperatures only, and are

discussed after the correction  $S\delta$  to the observed  $a/c$  values has been determined. In Table XXI are presented the results already obtained. The

Table XXI.

Gas.	$a^{\frac{1}{2}}$ .	A.	$A/a^{\frac{1}{2}}$ .	$\sigma$ .	B.	$w$
$N_2$	0.0518	759	$1.49 \times 10$	$3.10 \times 10^{-8}$	2.515	0.0327
$CO_2$	.837	1306	1.67	3.21	2.825	0.0067
$NH_3$	.893	1540	1.72	3.04	2.150	0.0141

$(\sigma, w)$  points are too few in number for an accurate determination of  $S$ , the values of  $A/a^{\frac{1}{2}}$  being uncertain, and the  $\sigma$  values close to each other. Allowing for the variation in  $A/a^{\frac{1}{2}}$ , the best value of  $S$  appears to be  $7 \times 10^6$ , while if we assume the variation in  $\delta$  from  $A/a^{\frac{1}{2}} = 1.7$  to  $A/a^{\frac{1}{2}} = 1.5$  should be the same as found with Miss Homfray's charcoal, the best value of  $S$  is  $9 \times 10^6$ . Taking  $S$  to be  $8 \times 10^6$ , we get  $S\delta$  to vary from 0.29 to 0.31. This value is so great that it is obvious that the correction must be introduced to the nitrogen and carbon dioxide values. The results are shown in Tables XVIII and XIX below.

Table XVIII.

Nitrogen.  $T_0 = 127$ . $B = 2.610$ .  $A = 736$ .

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	A
194	(2.20)	(2.20)	2.40	696
273	1.296	1.306	1.306	736
303	1.019	1.032	1.040	734
353	0.666	0.694	0.694	736
424.5	0.290	0.354	0.344	740

Table XIX.

Carbon dioxide.  $T_0 = 304$ . $B = 3.880$ .  $A = 1377$ .

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	A.
196.5	(5.04)	(5.04)	4.89	1407
273	2.917	2.917	2.923	1375
303	2.430	2.431	2.424	1378
353	1.783	1.785	1.780	1378
424.5	1.113	1.123	1.123	1375

# 310 *Adsorption of Gases at Low and Moderate Concentrations.*

The values of  $(1/T, \log a/c)$  with hydrogen do not lie on a straight line, but the curvature is less when the  $(1/T, \log a/c)$  points are considered. The value of the gradient between two of the points leads to a value of  $A/a^{\frac{1}{2}}$  much greater than any hitherto recorded, and this suggests an error in observation. The results of calculation are shown in Table XXII.

Table XXII.

Hydrogen.  $T_c = 39.$

$B = 1.11. \quad A = 311.$

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	Percentage error in $a/c$ .	A.
353	1.78	1.97	1.99	+5	304
273	0.23	0.30	0.25	-12	325
194	0.66	0.68	0.71	+7	305

Table XXA presents a summary for the corrected values of A and B.  $\delta$  is calculated from the relation  $w = S(\delta - \sigma)$ , assuming  $S = 8 \times 10^6$ . Comparing the values with those in Tables XV and XVI, the tendency for the values of

Table XXA.

Gas.	$a^{\frac{1}{2}}$ .	A.	$A/a^{\frac{1}{2}}$ .	$\sigma$	B.	w.	$\delta$ .
H <sub>2</sub>	0.0205	311	$1.52 \times 10^4$	$2.50 \times 10^{-3}$	1.11	0.13	$4.1 \times 10^{-3}$
N <sub>2</sub>	518	736	1.42	3.10	2.61	0.041	8.6
CO <sub>2</sub>	887	1377	1.64	3.21	3.88	0.0076	3.3
NH <sub>3</sub>	893	1540	1.72	3.04	2.15	0.014	3.2

$A/a^{\frac{1}{2}}$ , and hence of  $\phi(\tau_0)$ , to fall with  $a$  is again to be noted, carbon dioxide not forming an exception here. This tendency points to the necessity for the existence of a second relation, presumably dynamical, connecting  $a$  and  $\tau_0$ . The values of  $A/a^{\frac{1}{2}}$  appear to be slightly less in the present case, indicating that the attraction of the charcoal  $a_0^{\frac{1}{2}}$  is less. This may be connected with the smaller value of  $\delta$  and the greater surface S, which leads to a smaller thickness of the adsorbent—in this case only  $13 \times 10^{-3}$  cm. if composed of thin laminae.

There are no other observations available for the purposes of the present paper, so a summary of the results may now be given.

## *Summary of Part III.*

1. The form of the theoretical adsorption isostere for zero concentration has been established for a number of gases above their critical points.

2. The relationship among the constants is in good agreement with the theory based on the existence of a thin surface layer.

3. A new method of obtaining the relative internal cohesion of a gas is thereby presented.

4. The surface area of the adsorbent can be evaluated.

5. The range of molecular attraction may be determined, and in the cases considered is found to vary from 3.2 to  $4.1 \times 10^{-8}$  cm.

The author desires to express his thanks to Prof. James Walker, F.R.S., for his help in the presentation of this paper.

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*Address of the President, Sir J. J. Thomson, O.M., at the  
Anniversary Meeting, December 1, 1919.*

The losses of the Society since the last Anniversary Meeting have been very heavy. Fourteen Members on the Home List, and three Foreign Members, have died during the year, and among these are some who have for many years been most closely connected with the work of the Society, and whose discoveries and researches have for long been the glory of British science.

One of these, Sir WILLIAM CROOKES, had worked at science with untiring diligence and most conspicuous success for 60 years. A pupil of Hofmann, he became famous in 1862 by his discovery by the new method of Spectrum Analysis of a new element, thallium; this discovery won for him his election into the Society in the following year. In 1873 he again made a discovery which attracted universal attention, that of the Radiometer. The way in which he arrived at this discovery is as great a tribute to his genius as an investigator as the importance of the discovery itself. In the course of some chemical experiments, he observed certain irregularities in the weighings made with a very delicate balance; he followed these up, and at last traced them to forces acting on a surface exposed to radiation, and, with his unrivalled power of epitomising a discovery in a dramatic experiment, he summed the results of his work up in the well-known instrument, the radiometer or light-mill. Though subsequent research has not confirmed the theory by which he explained its action, the radiometer is a striking example of his skill as an experimenter, the thoroughness of his work, and his determination to leave no difficulty unsolved. His long-continued work

on the discharge of electricity through high vacua led to results of great importance, and the beauty and interest of his experiments did much to promote research in a region which has proved fruitful in results.

He had a singularly independent, original, and courageous mind; he looked at things in his own way, and was not afraid of expressing views very different from those previously considered orthodox. In not a few cases, notably in that of his views of radiant matter, time has shown that his ideas were much more in accordance with those which are now accepted than those commonly held by his contemporaries.

The Royal Society owes much to him for the services he rendered as Foreign Secretary and President, and especially for the papers which he communicated to the Society; these were delightful to those who heard them, and have increased in no small degree the value and interest of our 'Transactions' and 'Proceedings.'

We have lost another Past President, Lord RAYLEIGH, who continuously for the last 50 years enriched every branch of physics, with results of first-rate importance. Lord Rayleigh's output of work has rarely been equalled, either in distinction or in amount. He published nearly 400 papers; not one of these is commonplace, there is not one which does not materially advance its subject, and hardly one of them contains anything which requires correction. His discovery of argon is one of the romances of science. It might seem incredible, and, indeed, to some it was incredible, that, in spite of the study which for centuries had been made of the atmosphere, there should have been in it, quite unsuspected, such quantities of a new substance that the amount in a moderate-sized room is to be reckoned in kilogrammes rather than in grammes.

Time does not permit of even a sketch of Lord Rayleigh's contribution to science; a full account of these, it is hoped, will soon be forthcoming, but I cannot pass over without notice his 'Theory of Sound,' a model of a scientific text-book, for the clear and critical exposition it contains of the work of others, and for the value of his own contribution to the subject.

Lord Rayleigh possessed to a very remarkable degree the power of getting, in his theoretical as well as in his experimental work, at the very essence of the question, his judgment in scientific matters was unrivalled, and no subject ever passed through his mind without having difficulties removed and valuable ideas added.

To pass to other branches of his activity, he was Secretary of the Society from 1885 to 1896, and President from 1905 to 1908. He had from its inception (with which he had a good deal to do) taken the greatest interest in the National Physical Laboratory; he was Chairman of the Executive

Committee from its commencement until a few months before his death, and the success of the Laboratory is in no small degree due to his wisdom, interest and influence. He rendered great assistance during the war by the advice he gave in cases of exceptional difficulty, on which he was frequently consulted, and by his services as Chairman of the Committee on Aeronautics. He was for many years Scientific Adviser to Trinity House, and was one of the original members of the Advisory Committee on Scientific and Industrial Research.

GEORGE CAREY FOSTER, who had been a Fellow of the Society for fifty years, was one of its most beloved and respected members. His unfailing courtesy, his sagacity, his fairness and freedom from prejudice, made him an ideal councillor. He was one of those whose unobtrusive labours in the business and organization necessarily connected with the work of scientific societies have done much for the progress of science. He was the pioneer of the teaching of Practical Physics in this country, as in 1866, in two rooms in University College, London, he established the first Students' Physical Laboratory in England.

By the death of Mr. DUCANE GODMAN, at the age of 85, we have lost a great ornithologist and a benefactor of the Society, and one whose presence was always welcome at scientific gatherings. The 'Biologia Centrali-Americana,' edited by Godman and his life-long friend and colleague, Osbert Salvin, is, from its magnificent contributions to Natural History and Archaeology, a striking instance of the debt which Science owes to the labours of men who, like Godman, hold no office, but spontaneously devote themselves to the extension of knowledge.

The well-known physicist, Prof. WILLIAM WATSON, was Director of the Central Laboratory, B.E.F., from its establishment in 1915, soon after the first gas attack, down to the end of 1918. He did much in devising means of defence against an infamous method of warfare. He was frequently "gassed" himself, and his death after two months in hospital is attributed largely to the trying experiences he met with in the discharge of his duties.

Dr. A. G. VERNON HARCOURT, who died in August at the age of 65, was elected a Fellow of the Society in 1863, the same year as Sir William Crookes. He was endeared to many generations of Oxford men, a pioneer in the science of Physical Chemistry, and a very skilful experimenter. He was one of the Metropolitan Gas referees, and brought to its present state of efficiency the 10-candle pentane standard.

ALEXANDER MACALISTER, well known to many generations of Cambridge medical students, was a very successful teacher and worker in anatomy, and a man with exceptionally wide interests.

Dr. HENRY WILDE was a pioneer in the invention of the dynamo, and applied it on a large scale, more than 50 years ago, to the electro-deposition of metals and to searchlights for the Navy. A man of pronounced individuality, he interested himself in later life in the subject of terrestrial magnetism and the relation between the atomic weights of the elements. He founded the Wilde Lectureship in the University of Oxford.

Dr. JOHN AITKEN, who died but a few days ago, was, like Mr. Godman, an excellent example of an unofficial worker who made important contributions to science. His investigations on the influence of the presence of dust on the deposition of moisture have attracted much attention, both from the beauty of the experiments and the importance, both from the physical and meteorological point of view, of the results obtained. His scientific papers had a freshness, an originality, and a simplicity which gave them a peculiar charm.

I have also to record the loss of Prof. ADRIAN BROWN, distinguished for his researches on fermentation; Sir ROBERT INGLIS PALGRAVE, a distinguished statistician; Prof. TRAIL, of Aberdeen, a well-known botanist; LORD MACDONALD, and Sir EDWARD STIRLING.

Our Foreign Member, Prof. PICKERING, of Harvard University, was one of our most distinguished astronomers, and one who took a large share in the remarkable development of astronomical research in America in the last fifty years. His exceptional powers of organization enabled him to initiate and carry to a successful conclusion great schemes of astronomical research. To mention but one instance, at his observatory at Harvard about two hundred thousand photographs were taken and catalogued, showing all stars down to the eleventh magnitude and many fainter ones; these give a history, the only one that exists, of the Stellar Universe, and when a new object has been discovered its past history for many years has nearly always been revealed by these plates.

Prof. EMIL FISCHER had for long been one of the most famous of German chemists, the founder of a successful school, and a great teacher; his own work was of such importance that it has been said of him that by "his work on the sugars, the proteins, and the uric derivatives (each an enquiry of unparalleled magnitude and importance) he made biology on the chemical side a science."

The contributions to the literature of anatomy by our late Foreign Member, Prof. RETZIUS, of Stockholm, were unequalled by any one of his generation.

It was, as you may imagine, with the greatest regret, almost with consternation, that the Council heard from Sir Alfred Kempe that the state of his health obliged him to resign the office of Treasurer, which he has held for

20 years. It is difficult to find words adequately to express our indebtedness to him; by his sagacity, his long experience of the affairs of the Society, and his legal knowledge, he has rendered invaluable services in our councils and in directing the policy of our Society. He carries with him on his retirement from the office which he has so long and worthily held the thanks and good wishes of every member of the Society.

But this does not complete the list of our losses: it was with very great regret the Council heard from Dr. Schuster that he could no longer undertake the duties of Secretary. Everyone who has had the privilege of working with him during the strenuous years from 1912, when he took office, realises how much the Society owes to the unremitting work and zeal which he has devoted to the duties of his office, to the soundness of his judgment, and to his unstinted generosity. On him has fallen nearly the whole of the very heavy burden of the organisation of International Association necessitated by the war. We may congratulate ourselves that his activities in this direction will not terminate with his tenure of the Secretaryship, and that the question of International Science, in which he has so long been interested, and for which he has done so much, will still have the benefit of his work and guidance.

I have yet another loss to announce: the Council only a few weeks ago learnt with great regret that the state of Mr. Harrison's health was such that he could no longer discharge the very heavy duties of the Assistant-Secretaryship, an office which he has held for 24 years, the longest tenure in the history of the Society. I think all members of the Society will unite in thanking Mr. Harrison for the ability, zeal, and devotion to the interests of the Society which he has displayed so conspicuously during his long tenure of office, and will hope that the leisure to which he may now look forward will effect the complete restoration of his health.

This September Sir Richard Glazebrook retired, under the age limit, from the Directorship of the National Physical Laboratory. Few I think are privileged to see in such a striking and unmistakable form the success of their life's work as Sir Richard can, in the buildings and achievements of the National Physical Laboratory at Teddington, which have all been done under his direction. He leaves the Laboratory in the full tide of prosperity and with a splendid record of services rendered during the war.

The domestic events in the history of the Society have been so numerous that I have but little time for any other subject. I cannot, however, pass over without notice the remarkable result that was announced at our first meeting this session, that the observations made at the eclipse of May 29 showed that light was deflected, when passing close to the Sun, by an amount



which, within the somewhat wide limits of the experimental error, agreed with that predicted by Einstein.

The deflection of light by matter, suggested by Newton in the first of his *Queries*, would in itself be a result of first-rate scientific importance; it is of still greater importance when its magnitude supports the law of gravity put forward by Einstein, a law which has explained the long-standing difficulty of the motion of the perihelion of Mercury.

On Einstein's Law the velocity of light passing through a field of gravitational attraction depends upon the gravitational potential, and diminishes as the potential diminishes. Thus the gravitational field round the Sun acts like a refracting atmosphere, the refraction diminishing as the distance from the Sun increases.

Though there are some hundreds of theories of gravitation Einstein's is the only one which has predicted a result which has been verified by experience. On Einstein's, as on several other theories, changes in gravitational attraction travel with the velocity of light, and also the mass of a body varies with the proximity of other bodies.

In view of the statements in the press about the overthrow of the Newtonian Law, it may be well to point out that it is only in most exceptional cases, cases which are very difficult to realise, that the difference between the effects of the two laws is appreciable.

The modified theory of relativity by which Einstein arrived at this result is of remarkable interest and subtlety. The space around matter is on this theory distorted by an amount which diminishes as the distance from the matter increases, so that an observer in an aeroplane if he were provided with infinitely delicate instruments would, as he rose in the air, find the shapes of objects on the ground continually changing; and again the ratio of the circumference to the diameter of a circle would be changed to a minute amount by placing a weight at the centre of the circle. The laws of morality have been said to be a question of latitude, on Einstein's view those of geometry are a question of altitude.

On Einstein's view gravitation is due to a particle trying to find the easiest way through space distorted and disturbed in this way. We may put it as follows. The dynamical principle of Least Action, when applied to a particle moving through a space of this kind, would lead to a different path from that which would be pursued if the space were Euclidean, and this difference in path is that which would be produced if we supposed the space to remain Euclidean and the particle to be acted upon by an appropriate force. This force is what we call gravitational attraction. Thus we can represent the effect of this distorted space by the effects of suitable

forces, and I expect it will be found that even the most enthusiastic relativists will be tempted to think in terms of forces rather than in those of the geometry of non-Euclidean space.

If the distortion of space were very great, the customary methods of dynamics might lose their significance; and the question arises will, on Einstein's theory, the space inside an atom be so far from Euclidean that ordinary dynamical methods are unjustifiable? The answer to this question is, "No." There are two lengths which have special significance in connection with the atom; one of these is what we call the radius of the atom and is of the order  $10^{-8}$  cm., the other we call the radius of the electron and is about  $10^{-13}$  cm. Even at the smaller of these distances the gravitational potential due to the mass of the atom, and therefore the distortion from Euclidean space, would be exceedingly small compared with the corresponding quantities due to Earth at its surface, so that there is no special distortion inside the atom, except at distances from the centre, which are infinitesimal even when compared with the radius of an electron.

One point of interest in connection with any view we take about mass is that, on the electrical theory of matter, the massive part of the atom is invariably positively charged, so that any state of space which we associate with mass ought to involve something corresponding to a positive charge of electricity.

The determination of the consequences of Einstein's theory on the principles of relativity, where the ideas of space and time are so intimately correlated that time has to be treated as a fourth-space dimension, introduces us into a space of four dimensions which we cannot visualise, and whose properties are very remote from our experience. It is this which makes any general explanation of Einstein methods so difficult. To the analyst the difficulties presented by space of four dimensions are mainly those of an increase in the number of his symbols and equations; his difficulties begin when he has to explain his results to someone who is not an analyst. It is a remarkable and most interesting fact, from the point of view of either physics or metaphysics, that from such transcendental considerations as those I have indicated, should have emerged a result so closely connected with such a prosaic thing as that it is more tiring to go upstairs than down.

According to Einstein's theory the Fraunhofer lines in the Sun must be displaced towards the red. This effect, though looked for by several observers, has not been confirmed; but even should it turn out that the theory has to be greatly modified, or even abandoned, its conception and development will, I think, always be regarded as one of the great triumphs of human thought.

Another interesting consequence of Einstein's theory is the exceeding minuteness of structure which it demands from matter. The electron, with a radius of  $10^{-13}$  cm., carried our notions of the minuteness of some constituents of the Universe far beyond those associated with the older atomic theory, but the size of the centres of disturbance, which in Einstein's theory are associated with matter, bears to the size of the electrons about the same proportion as the size of the smallest particle visible under the most powerful microscope to that of the Earth itself.

I am afraid that the termination of the war has not brought to an end the difficulties in the way of scientific research in this country. Not the least of these is the difficulty and expense of procuring apparatus. It is perhaps surprising that under these circumstances the Government should have put obstacles in the way of the importation of philosophical instruments. Another very real difficulty is that the large increase in the number of students in our universities has greatly increased the educational duties of many of our most active workers, and so diminished the time they can devote to research.

The demands of war required large quantities of substances which previously were only obtainable in small quantities and at great expense. Prominent among these is helium, which can now be procured on a scale which, measured by Laboratory standards, is unlimited. Such supplies of helium put cryogenic research on a new footing and render possible investigations which promise to be of the greatest importance to many different branches of Science. It is greatly to be regretted that in this country, the birthplace of cryogenic research, we have no adequately equipped cryogenic laboratory.

We must now proceed to the presentation of the Medals.

The Copley Medal is awarded to William Maddock Bayliss, F.R.S.

Dr. W. M. Bayliss has been engaged in the investigation of physiological problems for the last thirty-five years. His work has ranged over a wide field. In his earlier papers dealing with the electrical phenomena associated with the excitatory state in glands and contractile tissues, he brought forward results which were at the time entirely novel and have formed the basis of all subsequent investigations. His paper with Starling on the electrical phenomena of the mammalian heart was the first to give the correct form of the normal variation, as confirmed by later investigations with the string galvanometer.

His work on vaso-dilator nerves and the part played by them in vascular reflexes, effected a revolution in our conceptions of nerve conduction and

showed that the law of Bell and Majendie, previously accepted as of universal application, did not express the whole truth, and that in fact a nerve fibre is normally the seat of processes which are both centripetal and centrifugal.

A third group of researches is represented by those on the innervation, intrinsic and extrinsic, of the intestines. In conjunction with Starling he showed conclusively that the movements of the intestine are under the control of a local nervous system, and even to the present time the intestines are the only organs in higher animals which have been shown to be the seat of a local nervous system capable of carrying out co-ordinated reflexes.

A fourth group of papers deals with the mechanism of the pancreatic secretion. Bayliss and Starling showed that this was effected by the production of a specific chemical messenger, which travelled by the blood, and not by the stimulation of nerve endings and the passage of impulses through nerves and the central nervous system. They showed, moreover, that this secretin was but a type of a whole group of substances which they designated hormones. The discovery of these hormones and the precise definition of their nature and of the conditions of their activity mark an important epoch in the development of our knowledge of the organs of the animal body.

His researches on the mode of action of enzymes and on the closely related questions with regard to the nature of colloidal solutions, have obtained universal recognition. His work on the osmotic pressure of colloids, as studied in solutions of colloidal dye-stuffs, is a model of the manner in which such investigations should be carried out.

The war led to Prof. Bayliss making a great advance in practical medicine. He studied the condition known as shock, which follows great loss of blood. The condition had previously been treated by the injection of saline solution, but the effect produced was characteristically transitory, and sometimes no benefit accrued at all. Prof. Bayliss, amongst other things, proved that perfused fluid to be effective must contain colloidal matter sufficient to give the osmotic pressure of the normal colloids of the blood. This and other results are given in his admirable work on Shock, which was published in 1918.

A Royal Medal is awarded to Prof. John Bretland Farmer, F.R.S., for his researches in botany, especially in the cytology and anatomy of plants.

His work is characterised by the fundamental importance of the problems worked upon ; thus his memoirs on the meiotic phase (Reduction Division) in animals and plants are of as great value to zoologists as to botanists, and his

conclusions and interpretations of the complex nuclear changes which precede the differentiation of the sexual cells have stood the test of criticism, and remain the clearest and most logical account of these very important phenomena; during the present year his views have received very full support. His papers, in collaboration with his pupil, Miss Digby, on the cytology of those ferns in which the normal alternation of generations is departed from, has thrown new light on problems of the greatest biological interest, and especially on the nature of sexuality. Further, in his cytological work on cancerous growths, Prof. Farmer has established the close similarity between the cells of malignant growths and those of normal reproductive tissue.

His physiological work also is of high quality. His observations on the circulation of protoplasm in plant cells, in the absence of oxygen but in the presence of light, may be referred to, and his most recent work on the water-conducting power of woody tissues opens up a new line of investigation.

A Royal Medal is awarded to Mr. James Hopwood Jeans, F.R.S.

Mr. Jeans has successfully attacked some of the most difficult problems in mathematical physics and astronomy. In the kinetic theory of gases he has improved the theory of viscosity, and, using generalised co-ordinates, has given the best proof yet devised of the equipartition of energy and of Maxwell's law of the distribution of molecular velocities, assuming the validity of the laws of Newtonian dynamics. He has discussed the theory of equipartition of energy from several points of view, and has shown that it inevitably leads to the Rayleigh-Jeans law of distribution of energy in the normal spectrum. As this law is found experimentally to be true only for long wave-lengths, Mr. Jeans has shown how in this and other cases, where the theory of equipartition is inadequate, the quantum-theory enunciated by Planck supplies the modification necessary to bring theory and observation into accordance.

In dynamical astronomy he took up the difficult problem of the stability of the pear-shaped form of rotating incompressible gravitating fluid, at a point where Darwin, Poincaré and Liapounoff had left it, and obtained discordant results. By proceeding to a third order of approximation, for which very great mathematical skill was required, he showed that this form was unstable. He followed this up by the discussion of the similar problem when the fluid is compressible, and concluded that for a density greater than a critical value of about one-quarter that of water, the behaviour is generally similar to that of an incompressible fluid. For lower densities the behaviour resembles that of a perfectly compressible fluid, and with

increasing rotation matter will take a lenticular shape and later be ejected from the edge. He has considered the bearing of these researches on Laplace's theory of the origin of the solar system, the formation of binary stars and the nature of spiral nebulae.

The Davy Medal is awarded to Prof. Percy Faraday Frankland, F.R.S., for his investigations in three sections of chemical science.

His early work on the illuminating power of burning hydrocarbons was considerable in amount and had the further merit of inspiring others in the study of combustion. He was one of the first after Pasteur to study seriously the chemical reactions which occur during the vital processes of numerous lower organisms, and to apply such reactions to the preparation of pure products. During the last 20 years he has devoted himself to the elucidation of the relationship existing between the chemical constitution and the rotatory power of optically active substances; the large amount of work which Prof. Frankland and his pupils have carried out on this subject has greatly advanced our knowledge of this relationship.

The Sylvester Medal is awarded to Major Percy Alexander MacMahon, F.R.S.

Major MacMahon's researches on the combinatory analysis and on subjects allied to the partition of numbers are of the highest value, and display great originality and invention. He has shown equal power in the discovery and treatment of the wonderful ranges of partition theorems which are derivable from the theory of elliptic functions, and of the similar theorems to be obtained by the application of analysis to purely arithmetical principles. In the difficult and almost untouched field of multiple partitions he has been a solitary worker; and no other mathematician since Sylvester has shown himself possessed of the special qualifications requisite to penetrate into the structure of number with the combination of insight and mathematical power that is apparent in MacMahon's papers.

The Hughes Medal is awarded to Dr. Charles Chree, F.R.S.

Dr. Chree has for many years devoted himself to the intimate study of the phenomena of terrestrial magnetism, notably those which are recorded by self-registering instruments. He has investigated the differences which occur in the diurnal variation on quiet or moderately disturbed days, he has studied the initial stages of magnetic storms, and has investigated various problems connected with the relation of solar phenomena and manifestations of terrestrial magnetism. These investigations are published in six papers in

the 'Philosophical Transactions,' and a number of others in the 'Proceedings of the Royal Society.' Perhaps the most notable result obtained is that called by Dr. Chree the "acyclic change." This manifests itself on taking the averages of quiet days, when it appears that the mean value of the magnetic force is not the same at the end as it was at the beginning of the 24-hourly period, but shows a difference which is always in the same direction. Owing to his knowledge and unique experience in the interpretation of magnetic curves, Dr. Chree is invariably consulted by explorers in the reduction and publication of observations obtained in Arctic and Antarctic Expeditions

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*A Study of Catalytic Actions at Solid Surfaces. II.—The Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel.*

By Dr. E. F. ARMSTRONG, F.I.C., and Dr. T. P. HILDITCH, F.I.C.

(Communicated by Prof. H. E. Armstrong, F.R.S.—Received August 18, 1919.)

It has been shown in the first part of this series that hydrogenation in the liquid state at a surface of metallic nickel is to be considered as effected by the temporary union of the unsaturated organic compound and of hydrogen with the nickel, followed by a breakdown of this intermediate system into nickel and the saturated compound.

This explanation is a development of the "intermediate compound" theory of catalysis first put forward by De la Rive\* and differs from the older view mainly in that it postulates an intermediate system of a very loose unstable type, similar to that produced between the natural enzymes, water (or oxygen), and the compounds attacked by the latter, during enzymic catalysis.

It evidently applies also to other cases of organic compound catalysis, such as the ketonisation of organic acids in presence of alumina, thoria, or other metallic oxides, and the dehydration of alcohols to ethers or olefines in presence of the same class of oxides. These catalytic actions have, indeed, been so explained by Sabatier and Mailhe,† on the basis of the simple "intermediate compound" theory.

\* 'Ann. Chim. Phys.,' vol. 39, p. 328 (1828).

† 'Compt. Rend.,' vol. 150, p. 823 (1910); 'Bull. Soc. Chim.,' vol. 13, p. 319 (1913).

The dehydrogenation of hydrocarbons by finely divided nickel or palladium seemed at one time to be more difficult to explain by theories of intermediate chemical association of the metal with the hydrocarbon, until the experiments described below had been undertaken, when we were able to correlate this type of action with those which have just been mentioned.

Sabatier and Senderens\* showed that cyclic hydrocarbons such as cyclohexane or methylcyclohexane are converted by means of nickel at 270–300° C. into benzene or toluene and hydrogen with a certain amount of methane as by-product. They explained the action as the withdrawal of hydrogen by the nickel on account of its tendency to form an unstable hydride.

In a later paper, Sabatier and Gaudion† have extended their work to a number of similar compounds at 350–360° C., and state that the presence of hydrogen is necessary for the decomposition to proceed satisfactorily.

They have also observed that, when pinene vapour is carried by a current of hydrogen over nickel at 350–360° C., the product consists of a mixture of cymene and cumene with a saturated hydrocarbon, probably a menthane, so that both dehydrogenation and hydrogenation were taking place simultaneously.

It is to be observed that, contrary to the hydrogenation process, catalytic dehydrogenation of these hydrocarbons is not by any means a complete operation, whilst the temperature at which it proceeds best, 270–300° C., varies from the optimum range given by Sabatier for the dehydrogenation of ethyl alcohol in presence of nickel, 180–230° C., and these facts suggest that the mechanism of each of the actions considered may not be of the same nature.

The evidence which we have obtained from time to time that metallic catalysts, during the hydrogenation process, interact primarily with the unsaturated organic compound, together with the resemblance of the whole process to enzyme action, led to the consideration whether the catalytic action, like that of certain enzymes, might not be reversible; in other words, whether specific compounds, although "saturated" in the ordinary sense, might be capable of interacting with the metal to form a system which would break down into a more stable equilibrium, consisting of hydrogen and a less saturated compound.

This speculation has to some extent been substantiated by the observation that hydrocyclic compounds of the nature of those studied by Sabatier, Senderens and Gaudion (*loc. cit.*), when heated in the liquid state with

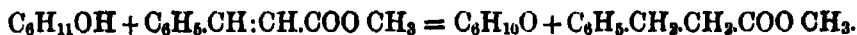
\* 'Compt. Rend.,' vol. 133, p. 568 (1901).

† 'Compt. Rend.,' vol. 168, p. 670 (1919).



nickel and an unsaturated compound at a temperature much below that employed by these workers and in absence of hydrogen, partially yield up hydrogen which is absorbed by the unsaturated component of the system.

The compound which, amongst the few we have studied, lends itself most readily to the action is cyclohexanol; at 180° C. a mixture of equimolecular parts of cyclohexanol and methyl cinnamate in presence of nickel may be transformed into one in which about 10 per cent. of the cinnamic ester has become hydrogenated to methyl  $\beta$ -phenylpropionate, according to the ultimate equation:—



Cyclohexanol.      Methyl cinnamate.      Cyclohexanone.      Methyl  $\beta$ -phenylpropionate.

According to the results of our experiments, it is necessary that both components of the system should be present in the liquid state, and no methyl  $\beta$ -phenylpropionate, or only very small traces, resulted when cyclohexanol was distilled through a mixture of methyl cinnamate and catalytic nickel. The dehydrogenation of cyclohexanol can be regarded as removal of hydrogen either from the hydrobenzenoid nucleus or from the secondary alcohol group present, and we have therefore examined other cases of hydrocyclic compounds in which the latter group was absent. Cyclohexane could unfortunately not be employed in the apparatus available owing to its high vapour pressure at the necessary temperature; distillation of cyclohexane through a mixture of methyl cinnamate and catalytic nickel led to a negative result, as in the similar distillation of cyclohexanol through the same mixture.

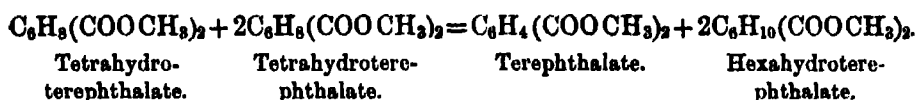
Dimethylcyclohexane (hexahydroxylene) and dihydropinene possess, however, sufficiently high boiling-points to admit of their employment in our apparatus, and it was found that, although little or no interaction with methyl cinnamate and nickel took place at 180° C., a certain amount occurred at 230° C. Similarly, a mixture of ethyl stearate and methyl cinnamate, when heated at 230° C. with catalytic nickel, gave a product containing small quantities of methyl  $\beta$ -phenylpropionate and ethyl oleate.

It was also found that a mixture of the cinnamic ester and catalytic nickel was absolutely unaffected by passage of a current of ethane, either at 180° or 230–240° C., but it is not possible to state definitely whether this is due to the incapacity of ethane to participate in the interaction, or to the fact that the ethane was not present in the liquid state.

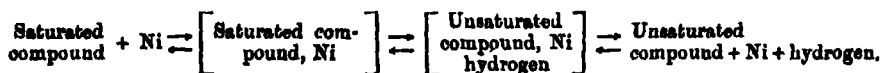
Employment was, however, found for the ethane, which had been used in the last experiment, by utilising it as the inert gaseous medium in the reaction vessel in many of the other experiments. In others carbon dioxide

was employed, but the interaction seemed to proceed much better in presence of ethane. It cannot be definitely stated that carbon dioxide is less suitable as an inert medium, since the difference may well be due to traces of some "anticatalytic" impurity in the carbon dioxide; the ethane would be free from the latter, having been prepared from ethylene by catalytic hydrogenation over nickel, and then passed through liquid methyl cinnamate at 180° C. in presence of nickel.

Another case of simultaneous dehydrogenation and hydrogenation was observed by Zelinski and Glinka\* in the action of spongy palladium on methyl tetrahydroterephthalate, when a mixture of methyl terephthalate and hexahydroterephthalate resulted. This is obviously of the same type as the action now described, differing only in that the transference of hydrogen is effected between different molecules of the same, instead of varying, compounds:—



The most novel feature of the present experiments would appear to be that simultaneous dehydrogenation and hydrogenation have now been effected at temperatures not far removed from the general optimum hydrogenation range of 170–180° C., and that hydrogen has been transferred from one compound to another, instead of from one molecule to another of the same species. Although we have no absolute proof that the mechanism of the change is not dependent on the production of hydrides of nickel, we consider that it is more natural to regard it as a further case of the catalytic equilibria which we have discussed above, depending on the formation of an intermediate system comprising the organic compounds, nickel and hydrogen:—



The equilibrium ultimately arrived at will depend on the resultant of the varying affinity for nickel of the saturated and unsaturated compounds involved.

The above doctrine of catalytic hydrogenation and dehydrogenation in the liquid state affords some explanation of the products obtained during the hydrogenation of unsaturated glycerides. Moore† has shown that partial hydrogenation of ethyl oleate causes the formation of ethyl stearate

\* 'Ber.,' vol. 44, p. 2305 (1911).

† 'J. Soc. Chem. Ind.,' vol. 38, p. 320 (1919).

and also of ethyl esters of isomeric forms of ordinary oleic acid, these being most probably ethyl elaidate and an ethyl "iso-oleate" derived from  $\Delta^{11,12}$  oleic acid.

The appearance of the elaidic ester, the stereo-isomeric form of ordinary oleic ester, is readily explained by the assumed equilibrated action between catalytic nickel and the ethylenic linkage, for on reformation of the constituents during the balanced action it is plain that either or both stereo-isomeric ethylenic derivatives might result.

The displacement of the "double bond" along the carbon chain is more difficult to understand, but since we have established that catalytic nickel is capable of bringing about dehydrogenation simultaneously with hydrogenation, it is possible to offer a tentative explanation of this abnormal isomerisation. As already stated, we have observed that transference of hydrogen from ethyl stearate to methyl cinnamate in presence of nickel proceeds to a very small extent at 230° C., and probably in the penultimate phase of our conception of the hydrogenation process, represented on p. 325 as [Saturated compound, Ni], the nickel, being already associated with the freshly produced ethyl stearate, is capable of active dehydrogenation at temperatures lower than 230° C. There would then be formed a dehydrogenated ethyl stearate, the hydrogen liberated being transferred to more ethyl oleate. The "dehydrogenated ethyl stearate" is, of course, according to this view, the ethyl  $\Delta^{11,12}$  oleate isolated by Moore, dehydrogenation proceeding preferentially at this point of the stearic acid chain of carbon atoms.

We are not concerned here with the reasons for this preferential action, and unfortunately the amount of transformation effected, even at 230° C., when starting from ethyl stearate and methyl cinnamate, is so small that it does not appear possible at present to produce sufficient of the dehydrogenated ester to isolate it in quantity and determine its constitution.

It is nevertheless suggestive that, as Moore has pointed out, the production of the isomeric form of oleic acid takes place to a greater extent the higher the temperature of hydrogenation, and is also more marked, at equal temperatures, with palladium, generally a more vigorous catalyst than nickel.

Moreover, his observation that the final ratio of "iso-oleate" (i.e., mixed elaidate and  $\Delta^{11,12}$  oleate), to ordinary ethyl oleate is different when ordinary ethyl oleate is the subject of hydrogenation from that obtained when ethyl "iso-oleate" is hydrogenated, is to be expected if this explanation is correct.

*Experimental.*

Methyl cinnamate was selected as the material to receive hydrogen for the following reasons:—

(i) It absorbs hydrogen in presence of nickel in the usual hydrogenation process smoothly and rapidly over the temperature range 120–240° C., without appreciable formation of by-products, the ethylenic linkage only being acted upon.

(ii) The separation of a mixture of methyl cinnamate and  $\beta$ -phenylpropionate is somewhat more readily effected than that of most respective pairs of ethylenic and saturated compounds; after removal of the other component of the system a preliminary separation was made by distillation of the esters in a vacuum, when with methyl  $\beta$ -phenylpropionate present, a mixture of esters relatively rich in the latter distilled at about 105–110° C./5 mm., the remaining methyl cinnamate being recovered at 115–120° C./5 mm. The enriched mixture was hydrolysed with caustic soda and a mixture of cinnamic and  $\beta$ -phenylpropionic acids thus obtained.  $\beta$ -phenylpropionic acid is freely soluble in cold petroleum ether, whereas cinnamic acid is very sparingly soluble, and a final separation was made by this means; the  $\beta$ -phenylpropionic acid so obtained was almost, but not completely, free from cinnamic acid, and melted in general at about 50° C. instead of 48° C., the true melting-point.

The catalytic operation was carried out by mixing at about 50° C., the desired proportions of methyl cinnamate and cyclic derivative with nickel catalyst, and displacing all air from the vessel by a current of ethane or carbon dioxide. The apparatus was then closed and heated at the experimental temperature whilst intimate mixing of the solid catalyst with the liquid was maintained. Subsequently the product was filtered from catalyst and then distilled, as described above.

The following experiments illustrate the results obtained during the investigation:—

*Cyclohexanol.*—The cyclohexanol was prepared by hydrogenation of phenol, and had been freed from simultaneously formed cyclohexanone by treatment with sodium bisulphite solution.

50 grm. of cyclohexanol and 80 grm. of methyl cinnamate were heated with nickel catalyst in an atmosphere of ethane at 180° C. for 1½ hours.

On fractionation of the filtered product at 10 mm. there were obtained:—

- (1) 36 grm., b.p. 58–60° C.
- (2) 30 grm. of liquid esters, b.p. 113–114° C.
- (3) 40 grm. of crystalline methyl cinnamate, b.p. 128–130° C.

Fraction (1) was extracted with a concentrated solution of sodium bisulphite, when the characteristic bisulphite compound of cyclohexanone, moderately soluble in the sodium bisulphite solution, was obtained; on regeneration of the ketone there resulted about 3 grm. of cyclohexanone.

A portion (10 grm.) of fraction (2) was hydrolysed, and eventually 1.5 grm. of  $\beta$ -phenylpropionic acid, melting at  $50^{\circ}\text{C}$ ., was produced. This corresponds to a total production of 4.5 grm. of  $\beta$ -phenylpropionic acid, or 5 grm. of methyl  $\beta$ -phenylpropionate.

In another experiment with 50 grm. each of methyl cinnamate and cyclohexanol, in presence of nickel catalyst, at  $180^{\circ}\text{C}$ . for 5 hours in an ethane atmosphere, about 12 grm. of the esters were hydrogenated.

It may be mentioned that the bromine absorption of the  $\beta$ -phenylpropionic acid obtained was in general about 2–3 per cent.

*Dimethylcyclohexane*.—This was obtained by repeated hydrogenation of xylene, followed by removal of unchanged xylene by a mixture of sulphuric and fuming sulphuric acid: it then boiled at  $129\text{--}132^{\circ}\text{C}$ .

50 grm. of methyl cinnamate and 25 grm. of dimethylcyclohexane were heated with nickel catalyst in an ethane atmosphere at  $180^{\circ}\text{C}$ . for  $1\frac{1}{2}$  hours, when it was found that no action had taken place.

A similar experiment was then made at  $230^{\circ}\text{C}$ . for about 1 hour. In this case slightly more than 2 grm. of methyl  $\beta$ -phenylpropionate were found in the filtered product.

*Dihydropinene*.—The pinene fraction of turpentine oil (b.p.  $155\text{--}157^{\circ}\text{C}$ .) was hydrogenated in the customary manner, the product being the desired dihydropinene (b.p.  $166^{\circ}\text{C}$ .).

On heating equal weights of dihydropinene and methyl cinnamate with catalytic nickel in a carbon dioxide atmosphere at  $180^{\circ}\text{C}$ ., no formation of phenylpropionate was observed; but at  $230^{\circ}\text{C}$ ., after analysis of the product in the usual manner, 3 grm. of  $\beta$ -phenylpropionic acid, melting at  $50^{\circ}\text{C}$ ., were obtained from 40 grm. of methyl cinnamate used in the experiment. The hydrocarbons recovered from this experiment were soluble to the extent of 30 per cent. of their volume in concentrated sulphuric acid, the original dihydropinene containing 8 per cent. soluble in this reagent.

*Ethyl stearate*.—The ethyl stearate was prepared by hydrogenation of pure ethyl oleate, and melted at  $34^{\circ}\text{C}$ .

100 grm. of ethyl stearate and 50 grm. of methyl cinnamate were heated in an ethane atmosphere at  $180^{\circ}\text{C}$ . for 3 hours without formation of any  $\beta$ -phenylpropionate. The recovered methyl cinnamate crystallised at once whilst the 90 grm. of ethyl stearate recovered absorbed 0.3 litre of hydrogen measured at  $18^{\circ}\text{C}$ ., on rehydrogenation.

A similar result was observed when the same proportions of the esters and catalyst were heated at 230° C. for 1 hour. On heating these proportions at the higher temperature for 5 hours, however, a small transference of hydrogen from stearate to cinnamate was evident. The products separated under 5 mm. pressure as follows:—

B.P. 105–108° C., 5 grm. mixed cinnamate and  $\beta$ -phenylpropionate.

B.P. 115–128° C. (mainly 125–126° C.), 24 grm. crystalline methyl cinnamate.

Residue, 97 grm. fatty acid ethyl esters, which re-absorbed 1.0 litre of hydrogen measured at 19° C. on rehydrogenation.

From the lower boiling fraction 0.8 grm. of  $\beta$ -phenylpropionic acid was obtained.

In another experiment, 100 grm. of ethyl stearate and 25 grm. of methyl cinnamate were heated with nickel catalyst in ethane at 250° C. for 1 hour, when a slight action occurred, about 0.5 grm. of phenylpropionic acid being isolated, whilst the residual ethyl stearate (after removal of all methyl cinnamate by distillation in a vacuum) absorbed 1.05 litres of hydrogen on rehydrogenation.

An experiment was also made at 180° C., the apparatus being initially filled with hydrogen, in order to ascertain whether a slight initial hydrogenation might induce the transference action at a lower temperature; the result was negative, about 1 grm. of  $\beta$ -phenylpropionic acid being obtained—an amount less than that possible to be obtained from the 400 c.c. of hydrogen present.

A similar attempt to induce the process with hydrogen in the case of dihydropinene and methyl cinnamate was equally unsuccessful.

*Errata in Part I (p. 137 supra).*

<i>Page</i>	<i>Line</i>	<i>For</i>	<i>Read</i>
138	9 and 10 from bottom	25 per cent. palmitin	5–10 per cent. of saturated glycerides.
144	14 from top	(Ni lead—CH : CH—)	(Ni, —CH : CH—).
144	In table, 2nd column	0.25	0.6.

*Tidal Friction in the Irish Sea.*

By G. I. TAYLOR, M.A.

(Communicated by Sir Napier Shaw, F.R.S.—Received December 4, 1918.)

## (Abstract.)

The rate of dissipation of energy at spring tides in the Irish Sea is calculated from the known formulæ for skin friction of the wind on the ground and the friction of rivers on their beds. The results range from 1040 ergs to 1300 ergs per square centimetre per second. The least of these is 150 times as great as Mr. Street's previous estimate of 7 ergs per square centimetre per second.

The rate at which energy flows into the Irish Sea is next calculated from the rise and fall of tide, the strength of the tidal current, and their phase difference over two sections taken across the North and South Channels. The rate of dissipation of energy is found to be 1530 ergs per square centimetre per second. This is in good agreement with the previous result.

It is next shown that this absorption of energy is sufficient to reduce the amplitude of the incoming wave to one-half, so that three-quarters of the energy of the incoming tidal wave is absorbed.

This absorption of energy explains most of the chief characteristics of the tidal phenomena of the South Channel to the Irish Sea, the velocity of the cotidal line, which is only about one-third of the velocity of the tidal wave, the angle through which the cotidal line turns in passing up the Channel, and the effect of Carnsore Point and Wicklow Head on the times of high water to the north and south of them.

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*A Linear Associative Algebra suitable for Electromagnetic Relations and the Theory of Relativity.*

By W. J. JOHNSTON, M.A., Assistant Professor of Pure Mathematics in the University College of Wales, Aberystwyth.

(Communicated by Sir Joseph Larmor, F.R.S.—Received August 28, 1919.)

Clifford has pointed out that geometrical algebras may be based on a system of fundamental units,  $i, j, k, o$ , etc., these units being alternate ( $ij = -ji, io = -oi$ , etc.), and the square of each unit being  $-1$ . It can be proved that such a system is associative.

Such an algebra based on four fundamental units,  $i, j, k, o$ , expresses in a remarkably simple manner the vector formulæ of Minkowski and the electromagnetic relations.

The four fundamental units, together with their products,  $ij, io$ , etc.,  $ijk, ijo$ , etc.,  $ijko$  each with the factors in a definite order and the scalar unit 1 give a linear associative algebra of 16 units. The scalar unit is commutative with the others, and the remaining 15 units may receive any interpretation, geometrical or otherwise, that is consistent with the distributive and associative principles.

The units  $i, j, k$  will now be interpreted as mutually rectangular unit vectors in Euclidean space, and the unit  $o$  as a unit vector in the fourth dimension perpendicular to each of the other three. For the present application the other units  $ij, jk, jo$ , etc., may remain uninterpreted.

The product of two vectors in four-dimensional space

$$xi + yj + zk + wo, \quad x'i + \dots$$

consists of two partial products. One partial product

$$(yz' - y'z)jk + \dots + \dots + (xw' - x'w)io + \dots + \dots \quad (1)$$

is Minkowski's "six-vector."

The other partial product

$$-(xx' + yy' + zz' + ww') \quad (2)$$

is a scalar.

Put  $w = ct\sqrt{-1}$ , where  $c$  is the velocity of light, and  $\sqrt{-1}$  is regarded as an uninterpreted symbolic scalar commutative with all the units  $i, jk, ijo$ , etc. Then the position of the point  $(x, y, s)$  at the time  $t$  is represented



by the extremity in four-dimensional space of the vector drawn from the origin

$$xi + yj + zk + wo = xi + yj + zk + ct\sqrt{(-1)o}.$$

If we suppose that the two vectors,  $xi + \dots$ ,  $x'i + \dots$ , are drawn from the origin O to two points P, Q in four-dimensional space, then the scalar (2)

$$= -OP \cdot OQ \cos POQ = (PQ^2 - OP^2 - OQ^2)/2.$$

$$\begin{aligned} \text{But } PQ^2 &= (x-x')^2 + (y-y')^2 + (z-z')^2 + (w-w')^2 \\ &= (x-x')^2 + (y-y')^2 + (z-z')^2 - c^2(t-t')^2, \end{aligned}$$

and similarly for  $OP^2$  and  $OQ^2$ . Thus the scalar (2) is invariant in the theory of relativity.

Let the partial product (1) be multiplied by the vector  $x'i + y'j + z'k + w'o$ , then we have two partial products. One is the sum of scalar multiples of  $i, j, k, o$ , and the other is the sum of scalar multiples of  $ijk, ojk, oki, oij$ . These are the two "four vectors" instanced in Prof. Conway's tract on relativity, p. 40.

A vector factor may be replaced by a differential operator. Put

$$\begin{aligned} \nabla_1 &= i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} + o \frac{\partial}{\partial t} \\ &= i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} - o \frac{\sqrt{-1}}{c} \frac{\partial}{\partial t}. \end{aligned}$$

$$\begin{aligned} \text{Then } -\nabla_1^2 &= \left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2 + \left(\frac{\partial}{\partial z}\right)^2 + \left(\frac{\partial}{\partial w}\right)^2 \\ &= \left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2 + \left(\frac{\partial}{\partial z}\right)^2 - c^{-2} \left(\frac{\partial}{\partial t}\right)^2. \end{aligned}$$

Let  $iX + jY + kZ$  be the force in free ether on an electrostatic unit,  $iL + jM + kN$  the force on unit magnetic pole in the electromagnetic system,  $\phi$  the scalar potential, and  $iF + jG + kH$  the vector potential. Then the operation

$$\nabla_1 \{c(iF + jG + kH) + o\phi\sqrt{-1}\}$$

gives a scalar part

$$-c \left( \frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} + \frac{\partial H}{\partial z} \right) - \frac{1}{c} \frac{\partial \phi}{\partial t} \dots \quad (3)$$

It is known that this vanishes.

The other partial product is

$$jkL + kiM + ijN - \sqrt{-1}(ioX + joY + koZ) \dots \quad (4)$$

This is the "six-vector" mentioned in Prof. Conway's tract, p. 41.

If we operate with  $\nabla_1$  on the expression (4) and the result is equated to zero, we obtain the eight equations

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z} = 0, \quad \frac{\partial L}{\partial x} + \frac{\partial M}{\partial y} + \frac{\partial N}{\partial z} = 0,$$

$$c^{-1} \frac{\partial X}{\partial t} = \frac{\partial N}{\partial y} - \frac{\partial M}{\partial z}, \dots, \dots$$

$$-c^{-1} \frac{\partial L}{\partial t} = \frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z}, \dots, \dots$$

These are Maxwell's equations in the Hertz-Heaviside form.

The expression

$$iF + jG + kH + o\phi\sqrt{-1}/c$$

may be defined as the "four-fold vector potential." This has virtually been done by Minkowski. Then the process just given is equivalent to

$$\begin{aligned} \nabla_1^2 (\text{four-fold vector potential}) &= \nabla_1 \{\text{expression (3)}\} + \nabla_1 \{\text{expression (4)}\} \\ &= \nabla_1 \{\text{expression (4)}\} \\ &= 0. \end{aligned}$$

Hence also

$$\nabla_1^2 F = 0, \quad \nabla_1^2 G = 0, \quad \nabla_1^2 H = 0, \quad \nabla_1^2 \phi = 0.$$

Other details may be similarly expressed. The operator  $\nabla_1$  corresponds to the quaternion operator  $\nabla$ ; and if it is borne in mind that  $ij$  is no longer replaceable by  $k$ , etc., the properties of  $\nabla_1$  are obtained by similar methods.

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*On Generalized Relativity in Connection with Mr. W. J. Johnston's Symbolic Calculus.*

By Sir JOSEPH LARMOR, F.R.S., Cambridge.

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The calculus presented by Mr. Johnston in the note printed above is so concise for the direct expression of the relations concerned in electrodynamic relativity, and involves so aptly the main relations of physics, that it may be profitable to consider it in further detail from that point of view. Maxwell had himself introduced quaternion notation into electrodynamics.

In the first place, as to how the essential idea of invariance can come in, it will suffice to illustrate from three dimensions, in which the vector to a point  $xyz$  is represented by the binary form  $ix + jy + kz$ . Hence  $i, j, k$  are symbolic units defined algebraically by the typical relations  $i^2 = -1$ ,  $ij = -ji$ ; but the further quaternionic relation  $ijk = -1$  is not assumed, for though  $(ijk)^2$  is necessarily unity, just as  $i^2$  is  $-1$ , the use of roots or fractional powers of operators is excluded. Now just as we can pass from a point  $xyz$  to another point  $x'y'z'$ , so also we can change from one trihedral set  $ijk$  to any other one  $i'j'k'$  possessing the same characteristic modes of combination. In fact let  $x'y'z'$  represent the same point  $xyz$  referred to this other set of Cartesian axes, their values being expressed by the usual equations for change of axes; then  $ix + jy + kz$  becomes on substitution  $i'x' + j'y' + k'z'$ , and it is readily verified that the set  $i'j'k'$  thus determined is of the same type as  $ijk$ . The formulæ so obtained for them are one general specification of such systems of units, irrespective of what value the product  $ijk$  may have. Extension of these ideas to  $n$  dimensions is natural and direct.

A self-consistent  $ijk \dots n$ -fold algebra has been developed, on geometric analogy, mainly by Clifford\* after Hamilton and Grassmann. In it the square of the difference of the vectors of two points, viz.  $(i\xi + j\eta + k\zeta + \dots)^2$  where  $\xi$  represents  $x_1 - x_2$ , etc., turns out to be the purely scalar quantity  $-(\xi^2 + \eta^2 + \zeta^2 + \dots)$ , and this suggest the geometrical interpretation. For it is the square, with changed sign, of the *distance* between the two points in Euclidean geometry, and so is invariant when the region is referred to a new set of unitary vectors. Now, the duality inherent in relative properties makes reference to a new trihedron  $i'j'k'$  equivalent to a rotation of the region, referred to the previous one  $ijk$ , except as regards the possible addition of a reflexion of the region in

\* 'Amer. Journ. Math.,' vol. i (1878); or W. K. Clifford's 'Mathematical Papers,' pp. 266-276.

a plane, which need not now be attended to. Thus the square of the distance expressed in this form is invariant for all displacements of the region, as referred to any frame  $ijk$ ; and this is sufficient to ensure that the geometry inherent in this consistent algebraic foundation is Euclidean, whatever be the number of dimensions. Invariant relations in the algebra connote constructions in that geometry, expressed directly without regard to any system of axes: all such quantities and relations as are evolved in Mr. Johnston's note are of this type, transcending special systems of reference.

An algebra of this kind remains valid when the scalar quantities involved in it, such as  $x, y, \dots F, G, \dots$ , are complex quantities instead of real, and this is a main feature of the application to physical fields. The  $\sqrt{-1}$  of the complex scalar cannot become mixed or confused with  $i, j, k, \dots$ ; although their squares are the same  $-1$ , their products remain explicit. Thus it is the same as if the scalar symbols were made complex only after the operations are finished.

The equations of electrodynamics are invariant as explained above for changes from any quaternary system  $ijk\omega$  to any other system  $i'j'k'o'$ , when one of the scalar coefficients, that expressing the time, is a pure imaginary. On this scheme a displacement in which time is implicated as the fourth dimension is the same thing as an alteration of translational velocity, in ordinary space, of the system as a whole. Just to the extent that invariance holds, is the formulation thus independent of any *constant translatory* velocity that may be ascribed to the whole system. This statement represents the limited degree of generalization that can arise on the usual scheme and be interpreted as non-essential of space and time, in a calculus like the present one.

In combining results of rotations about the same axis, it is the angles of rotation that are additive in the formulæ: thus, as Mr. A. A. Robb has pointed out, though velocities of convection in the same direction, such as  $v$ , are not additive, the corresponding angles represented by  $\sinh^{-1}v/c$  become so.

Having thus an auxiliary geometry of  $n$  dimensions of Euclidean type, it is the invariants, that arise in its calculus, that are the types of pure self-contained geometrical entity appropriate to such a hyperspace. The object of the Hamiltonian quaternion was to get rid of arbitrary frames of reference; the quantities that alone can occur in a quaternion analysis thus represent these invariants, viz., quantities resulting from additions and multiplications of complete vectors: and the question for that calculus is whether these suffice for geometrical reasonings, or whether an underlying scheme of reference such as  $ijk \dots$  is inevitable.

As the distance function is a sum of squares, this geometry is of the flat or Euclidean type. All simple types of geometry become flat in the

smallest regions; thus we may attempt to construct them by piecing together small flat regions, so as to form a uniform whole; and in this way Riemann has formed (in extension of Gauss) the elliptic and hyperbolic geometries by the method of the Calculus of Variations. Or we may consider the region around every material nucleus to be affected by its presence, and so to be non-uniform; and we may thus with Einstein propound the problem whether universal gravitation may be adequately or fruitfully represented by local deformation of space, instantaneously re-established whenever disturbance arises through convection of material nuclei, rather than by a field of stress which, on account of such very rapid restitution, could not be absorbed into the electrodynamic scheme of relativity.

Finally, the results of Mr. Johnston's note may be summarised. The "four-potential,"  $F, G, H, \phi$ , recognised by Minkowski,\* may be expressed by the symbol  $U$ , which represents  $Fi + Gj + Hk + W\phi$ ; and the usual spacial operator  $i\partial/\partial x + j\partial/\partial y + k\partial/\partial z + o\partial/\partial w$  is represented by  $\nabla_1$ . Then when  $\sqrt{-1}ct$  is put for  $w$  and  $\sqrt{-1}\phi/c$  for  $W$ , the expression for  $\nabla_1 U$  determines the conjoint electric and magnetic fields in terms of his notation by (4), viz.,

$$c\nabla_1 U = jkL + kiM + ijN - \sqrt{-1}(i\phi X + j\phi Y + k\phi Z),$$

where  $XYZ$  and  $LMN$  are the electric and magnetic intensities, the scalar part (3) vanishing in virtue of the electric field being devoid of convergence except at its sources. His expression for  $\nabla_1 \nabla_1 U$  consists of eight terms as follows:—

$$\nabla_1^2 U = \sqrt{-1}oA - iC - jC' - kC'' - \sqrt{-1}(jkoD + kioD' + ijoD'') + ijkB;$$

and its vanishing involves that of  $A, B, C, C', C'', D, D', D''$  separately, giving the eight equations of the electrodynamic field in free space in the order in which they are written in his note.†

Thus all is expressed in terms of two vectors,  $U$  and  $\nabla_1$ , in the unitary scheme typified by  $i^2 = -1$  and  $ij = -ji$ , but with no other restriction such as the  $ijk = -1$  of quaternions.

\* The procedure of Minkowski seems to have been, having identified electrodynamic relativity with invariance of the system as regards position in the fourfold continuum, to group and identify the physical quantities of the Maxwellian field as components of various 4-vectors and 6-vectors, constructed independently from the single fourfold vector potential so that their invariance is analytically recognisable. This gave rise to an algebra of the various types of vectors. The procedure in the present calculus is the reverse. The system of invariants natural to a four-dimensional flat continuum are immediately manifest in Mr. Johnston's application of Clifford's calculus; and the totality of them are identified precisely with the vectors of the electrodynamic scheme of Maxwell, with which they are co-extensive. The formal scheme of physical nature as regards electrodynamic and radiational phenomena is thus concomitant with the geometry of a single vector function in four Euclidean dimensions of space and time.

† These equations are set out *infra* on p. 345.

It is only in so far as a hyper-quaternion calculus can be framed, operating directly with hyper-vectors, such as  $\nabla_1$  and  $U$ , without any relation to a special unitary system of reference such as  $ijk \dots$ , that a method of direct relativity can be said to assert itself. Failing such a calculus, it is necessary to fall back on the indirect method, which cannot help using  $ijk \dots$ , but bases the relativity on the proposition that there is nothing to distinguish one such system from any other; the conclusion is, in substance, that if we could transcend the modes of representation of the physical world that are open to us, we should discover direct relativity. In this continual effort to transcend, the method of Variations on Riemann's foundation has been a substantial feature; the symbolic calculus now under consideration seems to constitute another direct help to hyper-spacial synthesis.

Here the sole function of the quantity  $c$  is to make  $c dt$  of the same physical dimensions as  $dx$ : by change of unit it may be reduced to unity. But the alternative mode of expression,

$$\nabla_1^2 U = 0, \text{ involving the vanishing of } \nabla_1^2 F, \nabla_1^2 G, \nabla_1^2 H, \text{ and } \nabla_1^2 \phi,$$

implies on the ordinary theory of space and time that  $F, G, H, \phi$ , and therefore the whole disturbance, travel out in three dimensions of space from located point-sources with definite velocity  $c$ , which thus enters as the velocity of radiation; while the permanence of the sources has to be adapted to the scheme by FitzGerald-Lorentz deformations of their collocation.

Thus a scheme of the kind above specified, however symmetrical and concise as a representation of a field of activity, seems not to be so effective in the representation of its sources. An electron or an atom is a singularity permanent though mobile in space; that quality is essential to the idea of matter. Whereas in the continuum of four dimensions the electron is represented, not by a singular point, but by a curved line (that of Minkowski) with a condition to be satisfied all along it. The element of time is in this respect an obtrusion; the compact mobile singular point in three dimensions of space seems to be the natural expression of permanent unchanging existence.

(Added October 20, 1919.)

*Analysis of Possibilities in Geometric Algebras.*—Restriction is at first made to three dimensions: this will illustrate the general case, though new features will there come in through the higher products. The position-vector  $R$  from the origin to the point  $xyz$ , which satisfies the criterion of a vector being an entity independent of orientation of co-ordinates, is represented, at first tentatively, by the bilinear form  $ix + jy + kz$ . When the system of axes of co-ordinates is altered  $xyz$  become  $x'y'z'$ : and, when we

write the usual geometric equations of transformation, and so introduce a new trihedron,  $i'j'k'$ , related in the contravariant manner to  $ijk$ ,

$$\begin{aligned}x &= l_1x' + m_1y' + n_1z', & i' &= l_1i + l_2j + l_3k, \\y &= l_2x' + m_2y' + n_2z', & j' &= m_1i + m_2j + m_3k, \\z &= l_3x' + m_3y' + n_3z', & k' &= n_1i + n_2j + n_3k,\end{aligned}$$

then the position-vector  $R$  is also expressed by  $R'$ , equal to  $i'x' + j'y' + k'z'$ .

By the known relations of Euclidean geometry, it is now easy to verify that the unitary system  $ijk$  does, in fact, remain invariant as to type, except that the product  $ijk$  changes sign when the system of axes undergoes perversion, represented symmetrically by reversal of sign of all the units. Thus, for the group of rotations without perversion,  $i^2 + j^2 + k^2$  is invariant, and the product  $ijk$  as above. But a binary product  $i'j'$  is not expressible in terms of like products  $ij, jk, ki$  unless  $i^2 = j^2 = k^2$ ; and then, provided further  $ij = -ji, \dots, \dots$ , it will have expression of type

$$i'j' = n_1jk + n_2ki + n_3ij,$$

here with no change of sign for symmetrical perversion. Thus the unitary relations  $ij = -ji, \dots, \dots$ , persist on transformation, so are invariant. Also  $(jk, ki, ij)$  is cogredient with  $(i, j, k)$  so that the quaternion simplification is suggested which avoids two kinds of vectors, making them identical by postulating that  $ijk$  is a scalar constant.

The square of  $R_1 - R_2$  is now  $i^2 \{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\}$ . As it must be invariant for change of trihedral axes, it is necessary that  $i^2$  be the same for all directions of the component vector  $i$ ; it must therefore be a scalar, say  $A$ . This involves and secures that the square of any vector is a scalar, say is the square of its tensor; and the vanishing of the tensor involves that of all the components of a real vector.

Thus the unitary system has been restricted to the form

$$\begin{aligned}i^2 = j^2 = k^2 &= A, & ijk &= B, \\ij &= -ji, & jk &= -kj, & ki &= -ik,\end{aligned}$$

involving three derived relations of type  $Aij = Bk$ .

It would seem at first that, to avoid complexities, the symmetric entity  $B$  must be scalar as well as  $A$ , and then we have  $B^2 = -A^3$ , so that both can be real only when  $A$  is negative. But this holds, as will appear, rather for quaternions than for pure vectors.

We can now further simplify the symmetric group of units by multiplying them all by the same scalar, viz., by any quantity of ordinary algebra, real or complex. If this multiplier is  $\sqrt{-A}$ , the plan of a spacial algebra is reduced to the form

$$i^2 = j^2 = k^2 = -1, \quad ij = -ji, \dots, \dots, \quad ijk = -1 \text{ or } +1.$$

The first alternative is the unitary scheme belonging to quaternions; the second alternative is the same scheme perverted symmetrically by change of sign of all the units.

A scheme with  $i^2 = j^2 = k^2 = +1$  cannot be obtained for the flat space except by multiplying each unit by  $\sqrt{-1}$ , which involves every component of every vector being a pure imaginary.

Perversion of a space (in the sense of Listing and Maxwell) is transformation into a new space, the mirror image of the former; thus change from  $i$  to  $-i$  is equivalent to a perversion. Two perversions in succession are equivalent to a rotation without intrinsic change; thus the quaternion unitary system is not altered by change of sign of both  $i$  and  $j$ .

The notation of quaternions, so far as regards pure vectors, was introduced into electrodynamic relations by Maxwell as a convenient means of exhibiting their independence of all special systems of co-ordinates, but not, at that stage, of all assignable systems of translatory convection. The earlier formulæ of direct attraction evolved by Ampère, Grassmann, and others were constructed on scalar ideas; but, as they implied instantaneous transmission, they were not affected by any finite motion imparted to the system, whether uniform or not. The effort to express the electrodynamic and other relations in terms of vectors independent of frames of reference in space, and also independent of uniform convection in space to which the formulæ of material dynamics and perhaps gravitation already give no response, is in the main the modern analytical problem of relativity.

*Limitation of Relativity to the Free Ether.*—The invariant scheme for an electrodynamic field does not constitute complete relativity. It is merely concerned with the changing field itself, of which the abiding discrete entities of nature are the sources. It is the relations between the latter that constitute the facts of existence: their own permanence throughout change of relations is implied and must be verified. Now the field of existence for this purpose is not that of  $x, y, z, t$ , but that of  $x, y, z$  alone: for matter and other permanent foundations exist not in time but irrespective of it. An electron is a singularity in space, whose essential qualities are independent of time. This may be claimed to be a true discrimination, which must prevent time being treated after the manner of another dimension of space. Events occur both as regards space and time, but the entities that substantiate these events, being the permanent constants in their mathematical representation, have no relation to time: phenomena are in space and time, and relate to substance, but that (unless we take matter to be a fleeting show) is the essential substratum into which time does not enter.

Thus, for example, for the equation  $\nabla_1^2 \phi = 0$ , the basic type of solution



$\{x^2 + y^2 + z^2\}^{-\frac{1}{2}} f\{ct - (x^2 + y^2 + z^2)^{\frac{1}{2}}\}$ , which in three dimensions expresses the fact of clean propagation without leaving a trail, such as exists for three dimensions but not for two, has in the four dimensions for its singularity or source by which it enters into the manifold, the line which is the axis of  $t$ . A point singularity would now belong to a point of space and to an instant of time: the field of which it is the nucleus, which is traceable back to it, would be regarded as introduced into the system through that point-source at a definite time. Such an instantaneous nucleus would be entitled to the designation of a *miracle*, as distinct from the usual permanent nucleus which would be a mobile *point of matter* or other abiding source. Such instantaneous nuclei may be amenable to treatment analytically by the methods of Green's memoir on potentials of ellipsoids in  $n$  dimensions: the simplest type of  $\phi$ , that which corresponds to the ordinary potential, is

$$A\{(x-p)^2 + (y-q)^2 + (z-r)^2 - c^2(t-\tau)^2\}^{-1},$$

having a singularity which at the instant  $\tau$  is at the point  $(p, q, r)$  and as time changes expands into an infinite source spread over a spherical surface, and thus is impracticable.

Ideas of propagation are, however, excluded in the fourfold space-time continuum, which presents a static map of the entire historical world-process at one glance. Though quantitative permanence as regards the inertial measure of matter evaporates, physical configurational permanence of the nuclei which constitute it would perhaps remain, while inertia is transferred hypothetically to energy. It is of interest in this connection to recall that when a permanent isolated material system is moving through space, and radiating away its thermal energy, while its total energy and momentum and inertia continually diminish, yet its velocity remains constant.\* These results follow on the usual electrodynamic principles; it is not a case of relatively transcending them, for the effects are of the first order in  $v/c$ : the velocity contemplated is thus velocity with respect to the æther. From the other point of view, such constancy of velocity is demanded by the relativity scheme as established for electrodynamics; for, if the velocity were retarded by the reaction of radiation, the system could not remain invariant when referred to a space-time frame moving along with itself. [This latter statement is thus the criterion on relativity principles that replaces the Newtonian first law of motion.†]

*Time contrasted with Space in a Permanent World.*—Analytically, varieties of geometric algebras may be obtained by altering the values of the squares of

\* See Poynting's 'Scientific Papers,' appendix added of date 1918.

† Cf. a cognate discussion in 'Proc. American National Academy,' 1917.

the various units between the alternatives  $+1$  or  $-1$ , or even by putting some of them equal to zero as in Grassmann's polar elements. The polar relations of type  $ij = -ji$  must not be tampered with. For if any of them were changed to the type  $ij = +ji$  the square of the distance of two points would no longer be invariant: we would have an algebra appropriate to some type of manifold, but that would no longer be a flat or Euclidean space whether real or imaginary.

The algebra of Hamiltonian quaternions of type  $wr + xi + yj + zk$ , in which one of the units  $r$  is the real quantity  $+1$ , is not a four-dimensional geometric algebra in the present sense, but is rather an algebra of two dimensions, viz.,  $ijk$  limited by  $ijk = -1$ , operating with another isolated dimension  $r$  of a different kind. To obtain in it a distance invariant in the four dimensions one must form the product with another quaternion, complementary to it as regards  $w$ , namely  $wr - ix - jy - kz$ , this product being  $w^2 + x^2 + y^2 + z^2$ . And similarly the operator  $\left(\frac{\partial}{\partial w}\right)^2 + \left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2 + \left(\frac{\partial}{\partial z}\right)^2$  is invariant only in this limited sense.

Thus the usual quaternion system can be developed: but it would appear to be rather an algebra of interaction between two types of vectors, one in three limited dimensions  $ijk$ , the other in the dimension  $r$ , these vectors combining as wholes according to the ordinary algebra of scalar quantities.

In a quaternary algebra,  $ijk\alpha$ , of direct geometric type, we cannot have  $\left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2 + \left(\frac{\partial}{\partial \alpha}\right)^2$  invariant, nor  $x^2 + y^2 + \alpha^2$ , unless it is a ternary geometric algebra combining with a unitary one  $\alpha$ . It then breaks up into an algebra of space and an algebra of time, the two combining by some scheme of rules such as those of the algebra of scalars. Except in this special case there cannot be permanent particles of matter or electrons belonging to the system (except as nuclei purely configurational) any more than there can be permanent spacial distances not involving time.

Electrodynamic relativity seems to be secured for the field in free æther by sacrificing them both: particles and electrons and space are resolved, so that only Minkowski's singular curves or "world lines" and their intersections—in a later form the intersections alone—survive. The material world vanishes in order that relativity may survive. It can thus be held to be more direct and practical, in relation to the complete expression of the order of nature, to persist so far as possible with the procedure expressed in terms of matter and motion, in the Newtonian manner; this requires and involves slight deformation of the material structure of measuring systems, and thereby is quite competent to secure, in relation to matter which alone can be

observed, the observed relativity that is otherwise interpretable by merging time with universal space into one interlocked manifold.\*

It may be noted that schemes in hyperspace and hypertime might be constructed in which time would be endowed with more than one dimension: there could be an algebra of time vectors operating with space vectors according to some scheme of laws, the simplest case being the mutual independence of time and space as above that goes with the laws of ordinary algebra.

Thus we appear to arrive again from the other side at the position previously asserted. Relations from their very nature must be between entities that possess features of permanence when the point of view (scheme of co-ordinates) is changed. Mutuality or relativity will be futile except as mere symbolism if these entities are not maintained. To establish the possibility of permanent material or electric systems it seems to be necessary to treat space by an algebra of its own distinct from time, in the manner originally enunciated summarily as a postulate, the cause of much misunderstanding at the time, by Newton in the 'Principia.'

Relations, which are the subject matter of knowledge, are changing in time: but there must be underlying things that are related, defined as of permanent type, even though in other respects known only through these relations, that is relatively. This duality, relations and entities related, appears to be unavoidable; the possibility of knowledge implies both.

The apparent present is merely a boundary between past history and future evolution. The past would thus be the real present that is with us, and memory the purveyor of the materials of systematic knowledge.†

But, whatever be the critical obstacles, the problem of probable interaction between gravity and electrodynamic fields, including rays of light, of course remains urgent; and if such connection is actually detected by the various astronomical determinations now in progress, data such as hitherto have been entirely non-existent will have been supplied for an attack on this deep-seated question.‡

\* This holds for the older experimental evidence of Michelson, Rayleigh, Brace, Fitzgerald and Trouton; the more recent astronomical evidence, involving the interplanetary spaces, cannot be so incorporated.

† It may be noted that the late Lord Rayleigh, in a Presidential Address to the Society for Psychical Research last April, hinted at his difficulty in understanding how past and future could possibly be related merely as North and South.

‡ This was written before it became known that the Greenwich and Cambridge astronomers, in their recent eclipse expeditions, had confirmed Einstein's prediction for the amount of the deflection of a ray of light by the influence of the Sun. It must be recognized that the theory has come to stay in some form or other. Its main implication, of instantaneous propagation of change in the constitution of space, seems to

The relation that  $ijk$  is a scalar, say  $-1$ , is not a necessary part of the geometric algebra: it is introduced in the mixed scalar and vector of quaternions in order to limit all the derived vectors to one type, and so get direct geometrical interpretation. But in the quaternary algebra, to restrict  $ijko$  to a scalar value would retain the algebraic geometry, while limiting its powers of representation; thus, for example, it would obliterate the expression of the electrodynamic scheme by combining its eight equations in pairs into only four. It would be really a ternary algebra with  $\pm o$  for the value of the product  $ijk$ .

The spacial algebra may in fact be elaborated in various ways. In the general case of  $n$  dimensions the distance of two points is invariant for algebraic geometries that involve all the relations  $i^2 = -1$ ,  $ij = -ji$ ; and this appears to be irrespective of how their unitary scheme may be completed by assigning laws and interpretations for triple and higher products.

May we say that all such completed systems represent flat or Euclidean spaces, and so are equivalent at bottom to the simplest single one that can be constructed, but that they differ as regards richness of detail? Viewed from the geometrical side the answer seems to be definite; a geometry of lines and distances appears to be quite feasible by itself on the basis of translation and rotation, as in Euclid, without advancing at all into special interpretations of the higher products, which could represent, through various schemes, quantities such as areas and volumes and their orientations.

As any invariant expression formed by multiplication of vectors is homogeneous in the units, though the reduction by substitution of  $-1$  for  $i^2$ , etc., makes it apparently not so, alteration of all the units by multiplying by the same scalar does not change the expression. It is therefore invariant as a whole, but not divisible into independent invariant parts; except that the parts of odd and even orders in the units are separately invariant, as with Clifford. In the expression for  $\nabla_1^2 U$  above, the two parts, one homogeneous of the first degree and the other of the third degree in  $ijko$ , cannot be other than conjugate components of a single generalised eightfold vector.

This process of evolving something completely different, an undirected scalar, from the interactions of directed vectors, was the startling innovation of the symbolic algebraic analysis. It perhaps had its ultimate suggestion, in much simpler form, in the imaginary of ordinary algebra and the Argand

be avoidable only on a psychological point of view which would assert that a portion of space is existent only while attention is concentrated on it. It can be managed, however, by including the varying space in a uniform space of higher dimensions, just as the deformation of a two-dimensional surface can be visualized as a whole in uniform space of three dimensions; cf. *infra*, p. 353.

diagram; this however involved a real and a complex or symbolic unit, whereas in a vector scheme, self-symmetrical, all units must be alike and symbolic.\* It can be developed on a purely logical unitary basis as de Morgan's "double algebra," whereas spacial geometry must run its algebra three abreast. Without the mode of representation as spacial threefold continuity, inherent in the mind, as the intuitive guide in an algebraic process, a calculus so remote from the usual chain of ideas of algebraic combination would have had small chance of emerging into light.

*On Imaginary Space.*—It seems legitimate, as above, to take each component of a general vector to be itself of the most general type of simple unidimensional algebra, namely, a complex quantity. But to do this with one of the components of the space vector is, in the usual terminology, to make that dimension of space imaginary. This would more consistently, in algebra, be effected rather by modifying the scheme of unit vectors that define the manifold, keeping the co-ordinate scalar multipliers real. Thus for the usual scheme of relativity, in which the fourth dimension, that of time, has to be a pure imaginary, instead of writing  $R = ix + jy + kz + (c\sqrt{-1})t$  to we could express it as  $R = ix + jy + kz + (ct)(\sqrt{-1} \cdot o)$ ; and similarly we would write  $U = iF + jG + kH + (\sqrt{-1} \cdot o)c^{-1}\phi$ ; pointing (as Mr. Johnston has remarked to me) to the introduction of a unitary system  $ijk'o'$ , the latter  $o'$  taking the place of  $o\sqrt{-1}$ , defined by the relations

$$i^2 = j^2 = k^2 = -1, \quad o'^2 = +1, \quad ij = -ji, \dots, \dots, \quad io' = -o'i, \dots, \dots$$

This contrasts with the quaternion group of four, scalar *plus* vector, in which  $o$  is merely the real numerical unit.

The analogy of the analytical manifold called an imaginary space to real space is so imperfect for practical purposes as to be almost fictitious when the space is flat. To realise it, generalisation is necessary into curved space such as that of a spherical surface: for example, the region within a closed ellipsoid has its boundary changed to one represented by an open hyperboloid, in flat space. As the new auxiliary manifold of relativity has nothing to do, except symbolically, with ordinary space, whether Euclidean or not, it is a more self-contained procedure to construct it independently on a basis of its own by an associative algebra of type  $ijk'o'$ .

We recapitulate the electrodynamic scheme on this basis, partly in order to emphasise another principle which it aptly illustrates.

The manifold in which the position-vector is represented by

$$R = ix + jy + kz + o'ct$$

\* See the discussion in Clifford's 'Math. Papers,' "On Biquaternions," especially the posthumous 'Further Note,' p. 385.

implies  $(R_1 - R_2)^2$  invariant, that is  $(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 - c^2(t_1 - t_2)^2$  invariant; it is thereby self-consistent and determined, in a form that can be visualised and so verified symbolically as an imaginary Euclidean space.

The invariant entity  $\nabla_1 U$ , where  $U$  is  $iF + jG + kH - o'c^{-1}\phi$  and  $\nabla_1$  represents  $i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} + o' \frac{\partial}{\partial(ct)}$ , is expressed as

$$\nabla_1 U = jk\alpha + ki\beta + ij\gamma + c^{-1}(io'P + jo'Q + ko'R);$$

for its value when set out at length in this way involves the electric force PQR and the magnetic force  $\alpha\beta\gamma$  of electrodynamics of free space, as expressed in terms of their partial potentials\*  $FGH\phi$ , and also involves the electrodynamic relation of convergence  $\frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} + \frac{\partial H}{\partial z} + c^{-1} \frac{\partial \phi}{\partial t} = 0$ .

The repetition of the same operation gives

$$\begin{aligned} \nabla_1^2 U &= ijk \left( \frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right) + ijo'c^{-1} \left( \frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y} + \frac{\partial \gamma}{\partial t} \right) + \dots + \dots \\ &\quad - o'c^{-1} \left( \frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y} + \frac{\partial R}{\partial z} \right) + i \left( \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} - c^{-1} \frac{\partial P}{\partial t} \right) + \dots + \dots \end{aligned}$$

Thus  $\nabla_1^2 U$  is expressed in terms of two partial vectors, with units  $ikjo'$  and their ternary products respectively, so named because they are only components of a complete complex, which in its entirety, and not as regards its separate components, enjoys the invariant property. The single equation  $\nabla_1^2 U = 0$  sums up the relations of the electrodynamic field in free space.†

[November 7, 1919.—The equation above, which expresses the vanishing of the scalar part of  $\nabla_1 U$ , viz.,

$$\frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} + \frac{\partial H}{\partial z} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0$$

is equivalent to

$$-\nabla_1^2 \phi = \frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y} + \frac{\partial R}{\partial z}.$$

\* The electromagnetic units of Maxwell's 'Treatise' are here employed, in which  $\text{curl}(F, G, H) = (\alpha, \beta, \gamma)$  and  $P = -\partial F/\partial t - \partial \phi/\partial x$ . In the Gauss-Helmholtz mixed electrostatic-magnetostatic system employed in Mr. Johnston's note, the first relation would be  $c \text{curl}(F, G, H) = (\alpha, \beta, \gamma)$ , and  $c$  occurs more symmetrically in the field equations. A rational way of getting rid of this embarrassing confusion between the units of practical science and the symmetrical Hertz-Heaviside modification is to eliminate  $c$  altogether in the mathematical analysis by making it unity. In the final results it could be restored by inserting in each term as a factor such power of  $c$  as is needed for uniformity of physical dimensions in the unitary system that is preferred.

† Observe that two of these eight relations are involved in the other six: this consistency is a test of the validity of the symbolic algebra.

The left side exhibits an invariant operator acting on a component of the invariant vector potential  $U$ , which is not itself invariant. Also the potential  $\phi$  is not cleanly propagated except in regions where the right side of the equation vanishes. As it has been known from the first\* that the distribution of charge is invariant, it follows that the expression on the right is not the measure of the charge though it vanishes in free space where there is no charge: that is because the element of volume changes on transformation as *infra*.

The symbolic calculus here under consideration adapts itself readily to the electrodynamic formulation for a space pervaded by electric flux and electric density expressed (after Lorentz) by continuous functions: and it is interesting to observe the successive stages of restriction. The invariance of the charge also emerges in a different way. Instead of  $\nabla_1^2 U$  vanishing, we assert an equation, which is invariant, of form

$$-\frac{1}{4\pi} \nabla_1^2 U = u_1 + jv_1 + kw_1 + o'c\rho + \text{zero},$$

the zero indicating that the vector-components of other type are to be made to vanish as they do identically. In other words,

$$\nabla_1^2 (F, G, H) = -4\pi (u_1, v_1, w_1), \quad \nabla_1^2 \phi = -4\pi c^2 \rho.$$

We may regard  $u_1, v_1, w_1, \rho$  as quantities to be interpreted. If we operate a third time with the invariant operator  $\nabla_1$ , on this simple vector  $-U/4\pi$ , the scalar part of the result is

$$-\left(\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} - \frac{\partial \rho}{\partial t}\right).$$

This quantity is therefore invariant for all frames of reference.† That being so, it is permissible to impose the physical restriction that this invariant value shall be zero. Then it asserts that  $(u_1, v_1, w_1)$  is some sort of circuital flow, or briefly of streaming, to which is added a convection of an electric density  $\rho$ . If it be further postulated that there is no such streaming, but only convection of the electric density, we have

$$(u_1, v_1, w_1) = \rho(x, y, z).$$

\* See 'Æther and Matter,' § 112.

† Other invariant vectors may be noted. Thus the mechanical force on the medium is expressed by three of a set of four components of the product  $-\frac{1}{4\pi} \nabla_1^2 U \cdot \nabla_1 U$ ; the Maxwellian stress system by components of the product of  $\nabla_1 U$  by a conjugate vector derived by changing signs of some of the units  $yjz'o'$ , and so on.

Thus now

$$-\frac{1}{4\pi} \nabla_1^2 U = i\rho\dot{x} + j\rho\dot{y} + k\rho\dot{z} + o'c\rho;$$

and its square with changed sign is

$$\frac{\rho^2}{dt^2} (dx^2 + dy^2 + dz^2 - c^2 dt^2).$$

Now the second factor of this expression is the invariant expressing the flatness of the four-dimensional continuum, hence the other factor, and so  $\rho/dt$ , must also be invariant. Also if  $d\tau$  is an element of ordinary volume  $d\tau dt$  is invariant, being the element of four-dimensional extension. Therefore  $\rho d\tau$  is invariant,\* which expresses persistence of value of electric charge when the reference is changed from one frame to another. It depends expressly on the postulate that all electric current is convection of charge. The inclusion of polarisation-charges would require special treatment]

In passing, it may be noted that  $-U^2 = F^2 + G^2 + H^2 - c^2\phi^2$ , so is scalar and invariant for change of axial system. Also, the scalar component of  $(\nabla_1 U)^2$  represents the volume-density of the Lagrangian function or of the kinetic potential in the four-dimensional space, being thus invariant itself, and securing by the Hamiltonian principle general dynamical invariance. Energy density is the scalar part of the product of two conjugates  $\nabla_1 U, \nabla_1 U'$ , and is not completely invariant.

But it is to be noted that, if the unitary scheme is restricted, after the manner that the quaternion scheme is restricted, by making the product of  $ijkl$  a scalar, the two partial vectors in  $\nabla_1^2 U$  lose their separateness of type, add together, and the complete electrodynamic formulation will be lost. The restricted system has been made too narrow, though still adequate for some other purposes of description in the manifold.

A set of units, with proper symbolic laws of combination, is what extends the scope of pure algebra from relations of linear measures to those belonging to more complex constructs in the continuum; but, when the scheme of their laws of combination is restricted, they may continue to be adequate for the simpler forms of the space relation, while they lose part of the power of expressing wider constructs through their combinations, and thus representing the interactions of physical phenomena arising in the space. While the quaternion restriction  $ijk = -1$  secures agreement with spacial intuition by involving only one kind of simple vector, the power of direct representation may thereby as here be much restricted.

\* Cf. E. Cunningham's exposition, after Minkowski, 'Principles of Relativity,' p. 105.



On the other hand, the products of second, third, and higher orders in a quaternary algebra  $ijkl$  are outside geometrical intuition; but Mr. Johnston has established with logical precision (as I understand) the validity of the associative principle in Clifford's algebra, and has also shown that the algebra involves, by introduction of twelve new auxiliary units, constructs of quaternion type, capable of including and representing Grassmann's various species of geometrical products.

It may be recalled that the Cartesian geometry involves already a symbolic algebra, that of the unit  $-1$  which reverses a vector. The algebra of ordinary complex imaginaries, as elucidated geometrically, is a binary one involving two symbolic units,  $-1$ , or say  $\alpha$ , and  $\sqrt{-1}$ , or say  $\beta$ , and the real unit  $\gamma$ , or  $+1$ , with the laws of combination  $\alpha^2 = \gamma^2$ ,  $\beta^2 = \alpha\gamma = \gamma\alpha$ ,  $\alpha\beta = \beta\alpha$ ,  $\beta\gamma = \gamma\beta$ . An algebra of polar units  $ijk \dots$  can be superposed on this one, as remarked above.

As already noted, the fact that the continuum  $ijkl$  is of only four dimensions does not preclude the formation in it of a generalised vector such as  $\nabla_1^3 U$ , having eight independent components. A parallel conception is the line-geometry, imagined also independently by Plücker, in which each line has four independent co-ordinates, or six symmetrical ones (the components in fact of Clifford's rotor) with two relations between them, though the space in which this geometry has its play has only three dimensions. As two lines (or forces) are not identical unless their co-ordinates all agree, so two eight-vectors cannot be identical, or the vector expressing their difference cannot vanish, unless all the components of the latter vanish separately. Or, again, there is the fourfold geometry in ordinary space, in which the spherical surface is the unit instead of the point, with combinations of its own: and so more generally. So also the vectors of the electrodynamic field have modes of combinations of their own, to which the scheme above presented is completely adapted.

In a real flat geometry represented by  $ijkl$ , dealing with pure vectors without the scalar part characteristic of quaternions, the square of the tensor of any generalised vector is a scalar represented by a sum of squares; thus the vanishing of the tensor—analogue to distance—involves that of the vector if it is a real one. But in an imaginary geometry such as  $ijkl$ , some of the squares are affected by the negative sign, and the vanishing of the tensor does not carry this result. Many theorems of determinacy which are valid for the real space fail for the imaginary one.

*The Specialised Relativity: its Limited Range.*—The converse mode of argument seems to lead directly to unexpected limitation of purely relative theories. For we can examine the degree of generality possible in a field of physical

activity, limited by only two characteristics: (i) effects are to be simply propagated across the æther, without leaving any trail, and all with the same standard speed when they do not travel instantaneously: \* (ii) uniform translational convection of the whole field of activity through the æther is not to produce any recognisable effect in the internal relations of that field.

The first characteristic requires that the distributions of scalar quantity specifying the field, say the functions  $F, G, \dots$ , should all satisfy the equation of simple propagation, which for three dimensions of space and one of time is of the type  $\nabla_1^2 F = 0$ . The second characteristic requires that in the manifold  $x, y, z, ct$ , these scalar quantities should be the components of a physical vector, say of  $U$ , equal to  $iF + jG + kH - o'c^{-1}\phi$ ; in this form they are virtually limited in number to four, the analysis for other conceivable types such as a six-vector, or for more than one vector  $U$ , being put aside as foreign to the actual physical type and impracticably complex. The operation  $\nabla_1$  or  $i\partial/\partial x + j\partial/\partial y + k\partial/\partial z + o'\partial/\partial(ct)$  is an invariant vector analogous to a position-vector, because  $\partial/\partial x, \partial/\partial y, \dots$  are transformed and combine according to the same type as  $x, y, \dots$  and it is the unique simple vectorial differential operator that is available. This equation  $\nabla_1^2 U = 0$ , which is the complete expression of simple propagation with uniform velocity, has also been shown, when constructed in two stages, to be the expression of Maxwell's electrodynamic equations; for they are formulated in terms of the vector components of  $\nabla_1 U$  as variables, these components representing the electric and magnetic forces of the field. For this purpose the scalar part of  $\nabla_1 U$  has been equated to zero in advance, being thus an equation of continuity, expressing that the convergence of the vector  $U$  vanishes. In any case, if that were not done, the vanishing of  $\nabla_1^2 U$  would in itself involve the vanishing of the gradient of this scalar convergence, and so make its value constant and therefore null. The two criteria, (i) and (ii), thus by themselves alone severely restrict possibilities, in an isotropic medium such as free æther with only one characteristic speed, to Maxwell's scheme of equations of the electrodynamic field.†

Expressed in Sylvester's terminology‡ the invariance of the binary linear form  $ix + jy + kz$ , which is made fundamental at the beginning of this note,

\* If there were two standard speeds, as there are for rotational and compressional waves in an elastic solid medium, their interplay would determine velocities of convection absolutely, so relativity would be excluded.

† This conclusion has been reached, as I now find, by Ph. Frank in 'Ann. der Physik,' vol. 35, p. 599 (1911), who ascribes it in more general form to H. Bateman, 'Proc. London Math. Soc.,' 1910. His analysis involves, after Sommerfeld, recognition of the products of the *Ausdehnungslehre*.

‡ Salmon, 'Higher Algebra,' §127.

requires that where  $(x, y, z)$  is transformed by any linear substitution  $(i, j, k)$  must be transformed by the contragredient substitution: this involves that if  $(x, y, z)$  is transformable by a rotation of a rigid geometrical system  $(i, j, k)$  is transformable also by a rotation, but one belonging to the conjugate (perverted) group. The characteristics of the polar units necessarily persist in this transformation; for it is already settled that on account of the invariance of distance the scheme can represent spacial relations.

The following treatment of the last discussed problem is a direct example. The transformation for which wave-motions with velocity  $c$  persist are those for which  $\nabla_1^2$  operating on  $U$  is invariant. Now  $x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} + w \frac{\partial}{\partial w}$ , where  $w$  is  $ct$ , is an invariant bilinear form, hence  $(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial w})$  are contragredient to  $(x, y, z, w)$ . Hence invariance of the operator  $\nabla_1^2$  involves invariance of  $x^2 + y^2 + z^2 - c^2 t^2$ ; that is, it obtains only under the Lorentz transformation, a result reached by Voigt by direct algebra a long time ago.

If the changes were very slow, or  $c$  very great, the field would be simply electrostatic, in which an electric nucleus repels another of the same kind. That is because the energy of the field is of static elastic type: if it were of the steady kinetic type there would be mutual attraction, as in gravitation.

It is because Mr. Johnston's rediscovery and adaptation of Clifford's calculus, though quaternary, is wider and more symmetrical than quaternions, that it is able directly to grasp and consolidate so much in the relations of physical analysis, though without the intuitive geometrical interpretation that quaternions enjoy. At the same time, like quaternions, it has the advantage of being condensed into one algebra involving unique modes of addition and multiplication of single variables: the separately defined products of other vector analyses arise in it compactly as components of the single product with which alone it has to be concerned.

I have been indebted to Mr. Johnston for criticism and corrections of this note. When it was written Prof. W. K. Clifford's papers relevant to the subject were not at hand. It seems desirable to add brief references to his work. He propounded his "Biquaternions" in 1873 as the algebraic operators which change the general position of a rigid body. Some time after, he became interested in general linear algebras with polar units, and recognised their relation to that special calculus. In 1878, the year before he died, he introduced a memoir\* entitled "Applications of Grassmann's Extensive Algebra," published in the first volume of the 'American Journal of

\* No. XXX in 'Math. Papers.'

Mathematics,' by the following pathetic sentences. "I propose to communicate in a brief form some applications of Grassmann's theory which it seems unlikely that I shall find time to set forth at proper length, though I have waited long for it. Until recently I was unacquainted with the 'Ausdehnungslehre' . . . I may, perhaps, therefore be permitted to express my profound admiration of that extraordinary work, and my conviction that its principles will exercise a vast influence upon the future of mathematical science." The paper determines, as he states, the place of quaternions and biquaternions "in the more extended system, thereby *explaining* the laws of those algebras in terms of simple laws;" it generalises them to higher dimensions and proves "that the algebra thus obtained is always a compound of quaternion algebras that do not interfere with one another." There is also a cognate posthumous fragment\* "On the Classification of Geometric Algebras." The prefatory introduction by H. J. S. Smith, pp. lv-lxvii, gives a sketch of the work, in which it is held, apparently with justice, that in bringing together Hamilton's and Grassmann's work Clifford had transcended both their points of view.

In the present note the algebra of Clifford is connected with spacial relations on the basis of the single criterion that it makes the square of the Euclidean distance of two points invariant for all transformations, for the reason that it is the square of the difference of their position-vectors. In quaternions distance enters in quite a different manner as a tensor. There are in Clifford's work indications, deserving fuller elucidation, how the flat or Euclidean geometry of four dimensions becomes elliptic geometry of three dimensions, with its more complex notion of distance, when the polar units are transformed to quaternion units in this way.

The apparent paradox in Clifford's algebra, on which H. J. S. Smith has put some stress, that although  $\epsilon_1\epsilon_2 = -\epsilon_2\epsilon_1$ , yet  $\epsilon_1^2 = -1$  and not  $= 0$ , is also present in quaternions, from which not improbably it was introduced; but really  $\epsilon_1$  and  $\epsilon_2$  are definite discrete entities, and the suggested transition to a limit when they are equal is not relevant, except within the narrower bounds of Grassmann's geometrical calculus of distances.

Clifford definitely separates the quaternary algebra based on units  $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ , defined by polar multiplication, together with  $\epsilon^2 = -1$  for each unit, into two algebras, one concerned with products of even order, the other with products of odd order. This is done by introducing a new unit,  $w$ , equal to the product of  $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ ; the unitary system thus becomes  $\epsilon_1, \epsilon_2, \epsilon_3, w$ , which is still polar, the only change of type being that  $w^2 = +1$  instead of  $-1$ , but

\* No. XLIII in 'Math. Papers.'

at the same time the orders of product terms are much reduced. For the algebra of even products, he recognises that this system is identical with his special calculus of Biquaternions. In the present physical application, this separation into two simpler algebras is however excluded, for  $\nabla_1 U$  is a product of even order while  $\nabla_1^2 U$  is of odd order.

In a condensed and powerful note on the motion of a rigid system left to itself without external force in a flat hyperspace,\* the idea of conservation of distance, which is made fundamental above, is not introduced. He develops kinematics on the basis of his polar unitary system as follows. A point is represented by the polar vector  $\rho = \sum x_k x_k$ , and its velocity enters through equations of type  $\dot{x}_k = \sum p_{hk} x_k$ , where  $p_{hk} = 0$ ,  $p_{hk} = -p_{kh}$ ; if, then,  $-2p = \sum x_k \dot{x}_k p_{hk}$ , the velocity of the point is  $\dot{\rho}$ , equal to the vector part of  $p\rho$ . He employs these formulæ to obtain the Eulerian equations of motion referred to axes travelling with the system, and therefore (be it remarked) self-contained without relation to external bodies; and he points out how their integrals are to be expressed in terms of the time by adaptation of the periodic relations subsisting in the groups of general  $\Theta$  functions. Thus the isolated rigid system in free rotation, relative to itself alone, provides its own absolute scale of time. The motion is evolved from instant to instant by means of the angular velocities of the body, referred to its own principal axes; just as a spacial extension is continued on Riemann's ideas from element to element by means of the values of its curvatures, or as a field of physical activity is continued stage by stage in space and time in the recent theories of relativity. If, as above, the rotational velocity is represented by time gradients of the changing polar units, referred to their own instantaneous positions, the  $p_{hk}$ , ... can be expressed as time gradients of  $l, m, \dots$

Clifford published in 'Nature' in 1873 a translation of Riemann's discourse on the construction, or rather continuation, of a space in terms of knowledge of its curvatures at the boundaries of its expansion; and, as Prof. Smith remarks, he "had imbibed the views set forth in it as a part of his intellectual nature." He had already contributed to the Cambridge Philosophical Society in 1870 a note of enthusiastic anticipation,† "On the Space-Theory of Matter," in which the atom was to be merely a mobile deformation of space just after the manner of the recent relativity formulation of gravitation.

\* 'Math. Papers,' XXV (1876), pp. 236-240.

† 'Math. Papers,' V. Riemann had already speculated that space need not be uniform around the molecules of matter.

*On Gravitational Relativity.*

[*Added November 20.*—The symbolic geometrical calculus which is the foundation of the previous discussion pertains only to the homaloid or flat continuum, in which the element of length  $\delta\sigma$  is expressed by the formula

$$\delta\sigma^2 = \delta x^2 + \delta y^2 + \delta z^2 + \delta w^2, \quad w = wt.$$

The phenomena of gravitation have been included by Einstein in this Minkowski scheme by altering slightly the expression for  $\delta\sigma^2$ , but so that it becomes expressed by the general quadratic function of the elements of length. This generalisation can still be brought within the range of the Clifford geometry by introducing into the analysis a new dimension ( $\xi$ ) preferably of space; so that

$$\delta\sigma^2 = \delta x^2 + \delta y^2 + \delta z^2 + \delta\xi^2 + \delta w^2, \quad w = wt,$$

with, of course, an additional component in the relevant vector potential  $U$ . For the relations of the electrodynamic field, those above expressed as existing between the components of the vectors  $\nabla_1 U$  and  $\nabla_1^2 U$ , are expressible, whatever be the number of dimensions, as relations of circulation\* of the type of Stokes' theorem, after the manner of Ampère's and Faraday's electrodynamic relations, which equate a flux across any sheet (binary locus) in the continuum to a circulation around its (linear) edge. Such relations, if true for the continuum as a whole, are valid also for any continuum of lower dimensions that is included within it. Now any

\* Cf. an analytical memoir by R. Hargreaves, 'Trans. Cambridge Phil. Soc.,' vol. 21, p. 107 (1908), which involved the germ of the general relativity relations as expressed in this manner. It seems, however, to be sufficient proof to observe that, on account of the vectorial character of the present analysis, on passing to a continuum of lower dimensions, every relation that involves only components of vectors, and their gradients, which exist wholly in that lower continuum, must remain true. [On working out the vectors in the electrodynamic fivefold (with interesting result), this statement proves to be true only for a flat section of it, as closer attention to the analogy of three and two dimensions would have warned. Thus the electrodynamic scheme, as well as gravitation, is modified from the usual form, but actually to a very slight degree. This analytic representation of the world-process as located in a curved section of a flat fivefold, involves, as now appears, other variables which are latent after the manner of the ignored co-ordinates of Routh and Kelvin in dynamics; and it is a question how far it agrees with Einstein's scheme. His method, cf. "Die Grundlage . . .," 'Ann. der Physik,' vol. 49, p. 812 (1916), is to transform the known electrodynamics of the flat fourfold into a curved fourfold determined so as to absorb gravitation, as if it were merely another phenomenon added on. But this electrodynamic construct may by Minkowski relativity be situated anyhow in the fourfold; hence its curved transformation ought, by the same relativity, to be situated anyhow in a flat fivefold which is a continuation of that fourfold. If this be allowed, there ought to be no disagreement, though this ultimate electrodynamic invariance is possibly hardly in strictness assured by Einstein's process.]

continuum of four dimensions, having a quadratic line-element, however complex, is expressible as a hypersurface in this homaloid continuum of five dimensions.\* If these considerations are correct, the Einstein generalisation, made with a view to include gravitation within his four dimensions, must be interpretable as the geometry of some type of hypersurface constructed in this extended homaloid of five dimensions. For the previous homaloid theory of Minkowski which ignored gravitation, this hypersurface, existing in the five dimensions, in which the world-process is represented, is flat; or more conveniently in some connections it may be taken as a closed region (hypersphere) of assigned uniform extremely small curvature, instead of the unlimited hyperplane. The problem then is to include in the scheme the influence—actually very slight in realizable cases—of gravitation; and this is to be done by recognising slight local deformations on this hypersphere in order to represent that effect. Now in the four-dimensional Minkowski map of the historical world-process, the rays of radiation are the curves of minimum length on the locus for which the analytic element of length  $\delta\sigma$  vanishes; and the paths of particles when gravitation was neglected were the curves (then straight lines in the flat) for which the length between assigned terminal points is minimum. If the hypersurface, which is very nearly uniform of very small curvature in the actual problem as presented in nature, can be so chosen that these two relations persist—namely, that the rays of light shall be geodesics on the locus determined by  $\delta\sigma$  vanishing, and the free orbits of particles with gravitation now introduced shall be the paths of minimum length on the hypersurface—then one way of absorbing the universal phenomena of gravitation, into the mixed space-time scheme which has arisen from and has transcended and obliterated the previous idea of relativity of positions and motions, will have been accomplished.

Viewed from this angle, the problem of the inclusion of gravitation, along the special lines of Hamiltonian variational dynamics on which a solution has been sought by Einstein, is one of map-making in these hyperspaces. We may illustrate by the simplest example, the one which originated the analytical theory of mapping. A map of the earth's spherical surface constructed on a plane expresses correspondence, point for point; but in other respects the correspondence is necessarily incomplete; for example, if angles are made to agree as in the familiar Mercator projection, the scale of correspondence of lengths must vary from place to place. The representation by a flat map cannot be complete; it can be achieved only as regards

\* This may be compared with Clifford's own development of his calculus, which subsumes elliptic or hyperbolic geometry of three dimensions under Euclidean geometry of four dimensions.

correspondence of certain chosen relations, and that only within a very limited range.

Now the problem developed by Einstein may be visualized as in a way the converse of this one. In the Minkowski four-fold continuum of space and time, which may be conceived as a flat or homaloid locus in our present auxiliary five-fold continuum, the scheme of electrodynamics and radiation exists, but the ordinary scheme of gravitation proves not to be adapted to it, when matters are tested by observation of nature to extreme refinement. Here existence means that its essential properties are independent of any particular scheme of measurement of them; as for instance the existence of a solid body in ordinary space is independent of the frame of reference with regard to which a measured survey of its form would have to be conducted: the source of this idea, which is the antithesis of relativity, is presumably our experience of the free mobility, without change, of the solid bodies around us. As just stated, in the flat or homaloid four-dimensional continuum of Minkowski, the phenomena of gravitation do not satisfy this criterion; the problem is to replace it if possible by some less simple type of four-dimensional continuum, constructed most conveniently as a hypersurface within our auxiliary flat five-dimensional scheme, in which both the electrodynamic and the gravitational theory shall exist in the sense above expressed.

The Minkowski world-process is mapped on a flat hypersurface, which can be conceived as existing in this hyperspace of five dimensions, but the gravitational orbits, though definite, are outside it, in the sense that they do not remain invariant, that their mode of specification has to be altered, when the axes of measurement in the hypersurface are changed. Can, then, this flat hypersurface be replaced by another one, so far as regards the actual problem of nature still very nearly flat, merely with very slight deformation in the neighbourhood of (so-called) gravitating masses, so that, while the invariance of electrodynamics is preserved, the same property shall be acquired by gravitation? One mode of acquiring it is that the free path of a particle, which, when gravitation was ignored, was always a shortest line on the flat, shall now be always a shortest line on the new hypersurface when gravitation is included. This is the correlative of the following problem in ordinary map-making: a representation of a given spacial configuration is constructed on the flat which is true to the configuration as regards an assigned limited number of properties; is it possible, by constructing the representation on a surface not flat but nearly flat, to make it true to the original as regards one more property?

The problem of Einstein in its widest generality, as one gathers, is not yet solved. But in the case that alone is amenable to practical test, in



which the adjustments are extremely minute, an approximate verification ought, of course, to be possible; and this is what Einstein has carried through, threading his way with great mastery of conception and analysis. The result obtained is that one can in this manner bring gravitation into the four-dimensional scheme, which is independent of axes of co-ordinates, at the cost of doing some violence to electrodynamics by introducing complications, to a degree, however, that is far too minute for experimental or observational scrutiny, and by doing violence to gravitation itself and its relations to light that happen to be just within the range of detection in three cases. It is as if one found that a cap would not fit exactly over a surface, but that a close fit could be forced by slight local stretching.

It is open to a critic to urge that this way of getting gravitation into the electrodynamic scheme proves nothing by itself, as Einstein apparently recognises, as to the unrestricted necessity or validity of a mixed space-time representation of the world-process; for it merely verifies some exceedingly small adjustments only to the first order of approximation, while a cosmological principle which aspires to the dignity of a law of thought must be absolutely true, without regard to approximation, for all magnitudes of change. That is, it would have to remain true if astronomical verification could deal with relative motions of many thousands of miles per second, instead of as actually with only a few tens. Viewed as demonstration, it is merely an approximate adjustment, and so carries very little evidence of universal unrestricted validity. Its true test had to wait some years for the opportunity of observation of nature. The adjustment of the slightly anomalous motion of the perihelion of Mercury taken by itself might well have been merely a coincidence. But, if in addition a prediction of the exact amount of deflection of a ray of light by the solar gravitation has been verified by the observers of the recent eclipse, as appears to be the case, then the point of view has most probably been established, though not necessarily in its present form. Even if the other prediction, of observable increase in the wave-lengths of light emitted in a field of gravitation, such as the sun or a star, proved to fail, the point of view must still claim attention: and the problem would be to amend the formulation once more, in one of the ways which may still be open, so as to force the scheme to include one other feature.

These considerations are submitted tentatively, with a view to getting far enough away from the complex analytical details of the gravitation theory to enable a judgment to be formed on its general physical aspect, and its relation to other recognised general principles of the scientific interpretation of nature.

One other remark, already hinted at, may be advanced. These theories arose out of the idea of the relativity of the positions and motions of material bodies. On the theory of an æther that idea was established demonstratively long ago, up to the order to which observation can test it, expressed either in terms of the original natural interpretation that motion through the æther affects slightly the dimensions of material bodies,\* or on the new conception of a mixed space-time foundation for representation of the system of nature. But in either case it is a very limited relativity; for it holds as regards translatory motion of the observer's system only when that motion is uniform, and as regards rotational motion not at all. It would appear that exposition of the new theory ought to get rid, as it can, of this glaring imperfection by ceasing to designate it as a theory of relativity at all; one would describe it as the theory of interdependence of space and time, such that time is virtually a fourth dimension interrelated with the other three dimensions of space, and *sui generis* only in so far as its measure is a number that is algebraically a pure imaginary. This statement seems to express the scope of the theory; by the theory both position and motion are transcended, in any sense that practically belongs to these concepts, and there seems to be no relevance in any further discussion about their relativity. The propagation of radiation is transcended also; its velocity becomes merely the dimensional multiplier that is required to make time homogeneous with length.

And again, a common interpretation of its point of view is that there can be no natural frame of reference, no æther. This appears to be almost repugnant to common-sense: for it would make the universe consist at best of a heap of unrelated particles in the void. And, in fact, these abstruse arguments on relativity cannot advance one step without the most elaborate frames of reference. The aim with which theory has to be content is to prove that we can get on equally well with a great variety of modes of expression of the natural frame of reference. It can even be maintained that this result is a strengthening rather than a destruction of the notion of an æther of space; for its aid cannot be dispensed with, while it is proved that its mode of intervention, possibly hitherto imperfectly appreciated, is so fundamental that it can be expressed in terms of a great variety of simple statements without mutual contradiction.

*Can a Field of Gravitation Disturb the Free Periods of a Radiation Spectrum?*

If this hyperspatial version of the Einstein gravitational theory is a valid presentation of physical reality, it hardly seems to warrant the usual

\* This mode of explanation would hardly be open for the recent astronomical verifications.

further conclusion that the free periods, as observed terrestrially, of the radiations emitted from the sun or a star, should be displaced towards the red end of the spectrum. At any rate further elucidation seems desirable: and with this in view we may strengthen our intuitional bearings by closer scrutiny of a parallel correlation applicable to spaces of two and three dimensions.

Geometry on a given curved surface is self-determined, in the manner developed by Gauss, in a binary set of curvilinear co-ordinates  $(p, q)$  and the expression for the element of length  $\delta s$  in the form

$$\delta s^2 = f\delta p^2 + 2g\delta p\delta q + h\delta q^2$$

in which  $f, g, h$  are known functions of position on the surface, and so are functions of  $(p, q)$ . If we can effect a transformation

$$\xi = F_1(p, q), \quad \eta = F_2(p, q),$$

so that the expression for the element of length becomes

$$\delta s^2 = k(\delta \xi^2 + \delta \eta^2),$$

where  $k$  is of course a function of  $\xi, \eta$ , then the equation for the shortest paths on the surface, which is  $\delta \int ds = 0$ , becomes

$$\delta \int k^{\frac{1}{2}} d\sigma = 0, \text{ where } \delta \sigma^2 = \delta \xi^2 + \delta \eta^2.$$

The quantities  $(\xi, \eta)$  may thus be taken as the co-ordinates of a correlative point in a plane: and a correspondence is established between the points  $(pq)$  on the curved surface and the points  $(\xi\eta)$  on a flat sheet which is in certain respects a map of it, corresponding elements of area being similar but not equal. A geodesic or shortest line on the surface corresponds to the orbit of a particle  $m$  on the plane, in a field of force whose potential  $W$  is determined by the equation of conservation of energy

$$\frac{1}{2}mk + mW = E_0;$$

for the variational equation has been transformed\* into the equation of Least Action  $\delta \int v d\sigma = 0$  in the field of force for which  $v = k^{\frac{1}{2}}$ . Correlative elements of length near any point are in the ratio  $k^{\frac{1}{2}}$ , and the elements of extension are similar in this ratio.

Now imagine, after the geometers, a two-dimensional intellect whose activities are confined to this curved surface. He may form a scheme of his surroundings either in terms of the co-ordinates  $(p, q)$  measuring the actual

\* As regards such correlations, see two papers, "On the Immediate Application of the Principle of Least Action to Dynamics of a Particle, Catenaries [Rigid Dynamics, Hydrodynamics], and other related Problems," 'Proc. London Math. Soc.,' vol. 15, (1884), in which this principle is worked out with examples. Cf. also the general analytical theory in Darboux, 'Théorie générale des Surfaces,' vol. 2, chap. vi (1889).

curved space, or in terms of the other co-ordinates  $(\xi, \eta)$  specifying more directly the correlated flat space. When the curved space is thus represented, the shortest lines on it are transformed into dynamical orbits on the flat. One might propound a problem, what should be the form of the surface in order that the orbits in the plane should belong to a field of gravitation? This seems to be an analogue, in two spacial dimensions, of the procedure of Einstein, except that possibly  $k$  has to be unity also. For it is to be remarked that what the intellect thus limited has to deal with is confined to the general type of connections, the mode of continuity, in the extension in two dimensions: there is no reason except convenience for a choice as to whether he should refer the binary manifold to a geometric frame of reference  $(p, q)$ , or to another  $(\xi, \eta)$ ; the latter is here the simpler frame, while the representation of the system is simpler on the former one. But when the intellect, originally limited, has learned to expatiate into the flat space of three dimensions, which we are familiar with as our own natural representation of space, things will have gained a wider outlook, and relations between the two modes of representation in terms of  $(p, q)$  and of  $(\xi, \eta)$  will have opened out.

Now let us transfer these considerations to the more complex physical problem. We have to contemplate an intelligence to whom the Minkowski continuum of mixed space and time of four dimensions, one of them imaginary, is intuitive. To him the historical world-process is spread out as one configuration situated in this Euclidean continuum. Whereabouts it is situated in it and how it is orientated is indifferent, just as the position of a material system of assigned internal constitution in ordinary space is indifferent; and that is what relativity has been reduced to in this scheme. It is at the choice of our four-dimensional intelligence to refer the historical world-process thus expanded before him, either to a flat fourfold space of reference analogous to  $(\xi, \eta)$  in the illustration, the space of Minkowski, having then to recognise gravitational forces and orbits modified under their compulsion within it, or else with Einstein to try whether it can be referred to a curved heterogeneous fourfold space of reference typified by  $(p, q)$  in the illustration, so that gravitational orbits shall become simply straightest lines so far as may be, and the physical notion of acceleration ascribed to a universal type of force thus replaced by a foundation purely geometrical or rather kinematic.

Neither of these representations is more valid than the other. To see them in direct relation to each other they must be surveyed by an intelligence to whom a five-dimensional mixed space-time scheme is intuitive, in which they are both contained as the curved surface and the plane of the illustration are

contained in space of three dimensions. In the Einstein analysis direct intuitive correlation is replaced by the surer method of algebraic correspondence. The co-ordinate system  $(xyz)$  for the flat hyperspace corresponds say to  $(x'y'z't')$  for the curved hyperspace, just as  $(\xi, \eta)$  corresponded to  $(p, q)$ , except that  $k$  need not be explicit. Their relation as determined by Einstein to the first degree of approximation that is sufficient for ordinary gravitation appears to be that, so far as regard the orbits, the constitutive spacial equation for the usual convention of flat space

$$\delta\sigma^2 = \delta x^2 + \delta y^2 + \delta z^2 - c^2 \delta t^2$$

corresponds to another for the presumed actual curved space,

$$\delta\sigma^2 = \delta x'^2 + \delta y'^2 + \delta z'^2 - c'^2 \delta t'^2,$$

where  $c'^2 = c^2 g_{44}$ ,  $g_{44} = 1 - 2c^{-2}V$  where  $\nabla^2 V = -4\pi\rho$ .

A geometrical quantity  $V$  arises of the type of a gravitational potential determining the density  $\rho$ , which latter may or may not prove to belong to a completely invariant mass: and  $\frac{1}{2}c'^2 = \frac{1}{2}c^2 - V$  as if the light also had a mass subject to gravitation.

The curved fourfold continuum is of the Riemann type, being flat as regards its infinitesimal elements of extension, as an element of an ordinary curved surface is flat.

We can compare events occurring in the element  $\delta x' \delta y' \delta z' \delta t'$  of the supposed actual curved continuum of Einstein as thus situated in the flat five-dimensional region, with events in the image of it which we form, in the corresponding element  $\delta x' \delta y' \delta z' \delta t'$  in the flat four-dimensional region in which a strained representation, involving gravitation somewhat modified,\* has been made. For these infinitesimal elements are both practically flat and so are comparable. The scale of ordinary space is not disturbed in the representation, but the scale of time is changed. For in the fivefold natural and presumably universal because simpler frame of reference, a Euclidean space-time continuum,  $c$  has its standard value: in the latter representation strained to a flat continuum of lower order, and so involving heterogeneous features interpreted as gravitation, it is changed to  $c'$ . But events are identical in the two representations, both flat and so directly comparable as regards these infinitesimal elements; hence as  $\delta x'$  is equal to  $\delta x$ , so  $c' \delta t'$  must be equal to  $c \delta t$ , where, as above,  $c'/c = 1 - V/c^2$ . The scale of the apparent time  $t'$ , involved in the conventional flat representation that is interpreted as a gravitational system is therefore different from that of

\* The modification of gravitation, and half its influence on rays of light, arise in the second approximation, in which, in a symmetrical field, the radial element  $\delta r^2$  in the value of  $\delta\sigma^2$  becomes affected by a factor  $1 + 2c^{-2}V$ . [This arises from an added postulate of conservation of fourfold extent: see a paper in 'Monthly Notices R. Astron. Soc.']

the standard time  $t$ , applicable to the world-system treated as non-gravitational and located as a four-dimensional non-flat configuration in the flat five-fold space. Where  $V$  is greater,  $c'$ , the apparent velocity of propagation in the flat element, is smaller, and corresponding apparent times are greater in inverse proportion. Thus the apparent periods of vibration of a hydrogen molecule in the field of high gravitational potential at the sun are greater than their normal periods; but on account of the smaller apparent velocity of propagation  $c'$ , the wave-lengths of the radiation emitted from it remain normal and constant throughout its course. When this radiation has travelled to a place of null gravitational potential, its apparent velocity will have fallen to the normal value  $c$ , and its period also will thus have become normal. Thus, if the superior intelligence that can visualize the five-dimensional manifold in which the true transcendental system and its gravitational representation both subsist, makes a comparison between them, he will recognise that they are merely referred to different scales of time, so that events appear to change more slowly in a region in which there is a higher gravitational potential when flatness is asserted and the fiction of gravitation therefore introduced. Thus, possessing his standard of normal time of the fivefold space, he will recognise that a molecule of hydrogen vibrating in a region near the sun emits radiations of slightly longer periods, as apparent in the gravitational scheme, than a like molecule vibrating in a terrestrial laboratory. This super-intelligence, with his transcendent powers of comparison, will thus recognise on the forced flat interpretation of the universe, a gravitational influence on the periods of free vibrations of a molecule of given material, which is eliminated when the real kinematic curved representation replaces the apparent flat and gravitational one. But the opportunities open to him are not those available to actual mundane spectroscopic verification: what is there immediately determined is not the period of vibration of a hydrogen molecule in the sun—that is beyond our reach—but the period of the waves emitted by it *as these waves pass the earth*. As the gravitational potential near the earth is comparatively small, and does not change much in the course of its annual motion, it would seem, at any rate subject to correction, both that observed spectral periods may be taken as constant throughout the year, and that as observed in the same locality there is no difference between light from the sun and light from a terrestrial source. Because in corresponding small elements of the related fourfold extensions spacial measurements agree, and the events are identical, all times of the systems must be correlated also, but in a ratio which varies from element to element.

The object of merging gravitation in a strain of the mixed space-time frame would thus be reduced to securing relativity, in the highly sublimated sense

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The object of merging gravitation in a strain of the mixed space-time frame would thus be reduced to securing relativity, in the highly sublimated sense



that the four-dimensional non-flat construction which presents the world-process at a glance is independent of its position or orientation in the five-dimensional flat electrodynamic construct, or rather as we could name it, in which it is contained, as a surface is contained in ordinary space. But on forcing this presumably more ultimate formulation into a four-dimensional scheme of the simple flat type, there proves to be a residual want of fit which cannot be got rid of, and has to be recognized as a new feature or property of nature, namely, gravitation in a very slightly modified form, which thus interferes slightly with the rays of light and even with the fundamental electrodynamic relations. But it does not seem to be clear as yet, unless the present expository process turns out to be a failure, that the periods of natural radiation can properly be asserted to be modified by a gravitational field in any-observable manner. As remarked for the introductory illustration, the linear element  $\delta s$  was there not necessarily invariant. In the present type of exact hyperspatial correspondence, it is just such invariance that causes the strained representation involving a changing scale of local time. In the application to actual gravitation the factor analogous to  $k$  is taken at its very approximate value unity. If it could be exactly unity (actually the relation is even not quite isotropic) this invariance of the hyperspatial element of length would provide perhaps a portable infinitesimal measuring rod for comparisons, which would not alter its length when its direction is changed, thus making comparisons thinkable without requiring the merging of the system in the wider auxiliary Euclidean spacial system of five dimensions as has here been done.

Wider possibilities of syntheses with  $k$  different from unity arise, but they would be more complex, vitiating the directness of correlation with the flat time-space scheme that is assumed, perhaps only provisionally, in ordinary physics, and possibly doing further violence to the latter and to the electrodynamic relations which it involves.

Thus we postulate a fivefold electrodynamic potential and its concomitant electrodynamic vector-systems in the Euclidean auxiliary space  $(x, y, z, \xi, \text{etc.})$ . Then any section of this space and its vector-system is a hypersurface of four dimensions of the same Minkowski type as that system itself, and represents a possible electrodynamic world-process; including implicitly its gravitation, which would become apparent only when the hypersurface, actually already nearly flat, is forced into representation on a hyperplane.

It is, of course, a very striking feature that Einstein's theory of gravitation not merely forces the Newtonian law into the impress of a relativity mould, but that it even evolves that very law in the form of its Laplace-Poisson characteristic equation, from a relativity representation in fivefold Euclidean

space which does not contain any such extraneous feature. But also, viewed from the other side, in extensional analysis of this type appropriate to isotropic Euclidean manifolds, the vector operator  $\nabla$  and its powers are the fundamental ones, so that it is not really very surprising that gravitational analysis can be linked up with a theory of deformable space.

Finally and again, this re-statement of theories of relativity as relations of correspondence in space and time, by aid of uniform auxiliary manifolds of higher dimensions, may appear retrograde: in the earliest phase relativity was just such correspondence.\* But it has the advantage of getting rid of the very puzzling auxiliary apparatus of local timekeepers, and their changes of rate when moved about. And, moreover, it is not, in fact, possible to do without a scheme of space and time; relativity merely asserts in various ways that its final specification so far eludes our powers that a large number of partial modes of specification can be employed indifferently over a wide range of problems.

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*On the Variation with Frequency of the Conductivity and Dielectric Constant of Dielectrics for High-Frequency Oscillations.*

By G. E. BAIRSTO, D.Sc., D.Eng.

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1. *Introduction.*

Although we have a certain amount of knowledge regarding the variation of the conductivity of dielectrics with frequency for comparatively low frequencies, within the telephonic range, say, up to 5000 per second, where the conductivity is in general a linear function of the frequency, it cannot be said that any information exists at present as to what happens when we extend the range of frequencies up to those employed in radiotelegraphic work. That energy is dissipated in condensers used in oscillation circuits has been known since 1861, when W. Siemens† pointed out that the glass of a Leyden jar became heated on charge and discharge. Threlfall,‡ extending

\* Cf. 'Æther and Matter,' chap. xi (1900). Here in cognate manner the five-dimensional space-time foundation is introduced in order to provide the necessary standards of time and space, which, even though provisional, are indispensable.

† 'Berlin Akad. Monatsber.,' October, 1861.

‡ 'Phys. Rev.,' vol. 4, p. 57, and vol. 5, pp. 21 and 65.

the early experiments of Arno, working with a rotating electrostatic field, found that under these conditions there was no hysteresis loss at  $10^7 \sim$  per second in the dielectrics he employed: ebonite, glass, and sulphur. At somewhat lower frequencies of the order of a million a second, several observers have made measurements of the energy dissipated, and find that condensers have an appreciable decrement. Reference may be made to the following: W. Hahnemann and L. Adelman,\* G. Dupreux,† J. J. Stockley,‡ M. Wien,§ J. A. Fleming and G. B. Dyke,|| L. W. Austin,¶ E. F. W. Alexanderson.\*\*

Most of the measurements were made at working voltages, so it is impossible to say how much of the energy loss is due to brush discharges and how much to a true dielectric conductivity. Moreover, the measurements have generally been confined to some particular frequency. The object of the experiments to be described below was to measure the conductivity of the dielectric over a wide range of frequency, employing continuous oscillations of sine wave form, and of low voltages.

Apart from the importance of the subject in connection with the properties of dielectrics in general, measurements of this kind are of value in another direction, viz, in the theory of the propagation of electromagnetic waves over the earth's surface. Before the theory as developed by Zeuneeck and others can be applied to practice, we require to know the values of the dielectric constants and conductivities of the constituents of the earth's crust, and the explanation of many anomalous effects which at present are but little understood, would in all probability be cleared up if we were in possession of these data for certain regions of the earth's surface. Loewy,†† with this object in view, has made an extensive series of such measurements, but only with direct currents (D.C.), which we now know gives values of the conductivities which bear no relation to conductivities as

\* "Losses in Condensers, and Damping in Wireless Telegraph Circuits," 'Electrotech. Zeit.', vol. 28, pp. 988 and 1010 (1907).

† "Oscillatory Discharges of Condensers," 'Electrician,' vol. 38, p. 107 (1909); or 'Science Abstracts,' 12 B, No. 906 (1909).

‡ "Effect of Temperature on Damping in Glass Condensers," 'Schweiz. Electrotech. Zeit.', vol. 6, p. 309 (1909); or 'Science Abstracts,' 12 A, No. 1441 (1909).

§ "Damping in Oscillatory Circuits," 'Ann. der Phys.,' vol. 29, 4, p. 679 (1909); or 'Science Abstracts,' 12 B, No. 1596 (1909).

|| "Energy Losses in High Frequency Circuits," 'Proc. Phys. Soc.,' vol. 23, p. 117 (1911); or 'Science Abstracts,' 14 B, No. 384 (1911).

¶ "Condenser Losses at High Frequencies," 'Journ. Wash. Acad. Sci.,' vol. 1, p. 143 (1911); or 'Science Abstracts,' 15 A, No. 199 (1912).

\*\* "Dielectric Hysteresis at Radio-frequencies," 'Proc. Inst. Radio. Eng.,' vol. 2, p. 137 (1914).

†† 'Ann. der Phys.,' vol. 13, p. 125 (1911).

measured with alternate currents (A.C.). Even at telephonic frequencies the alternate conductivity is much greater than the D.C. conductivity; at radio-telegraphic frequencies the differences become enormous. As a small contribution to the subject, the author has therefore included two typical constituents of the earth's crust in his measurements, viz., slate and marble.

## 2. Apparatus and Methods of Measurement.

The method of measurement adopted is based upon the resonance of a leaky condenser. Two condensers, one the unknown leaky condenser under test, and the other a standard air condenser shunted with a variable high resistance, are alternately placed in series with an inductance, and each adjusted for resonance with a primary source of oscillations, and also for the same maximum current in both. Under these circumstances, the capacities of the two condensers will be the same, and the shunted resistance will be equal to the reciprocal of the conductance for the frequency used during the experiment. Now it is exceedingly difficult to obtain a perfectly *steady*\* source of undamped alternating currents of high frequency. The condition of equality was therefore determined by means of the specially designed commutator shown in fig. 1. This commutator, driven by an

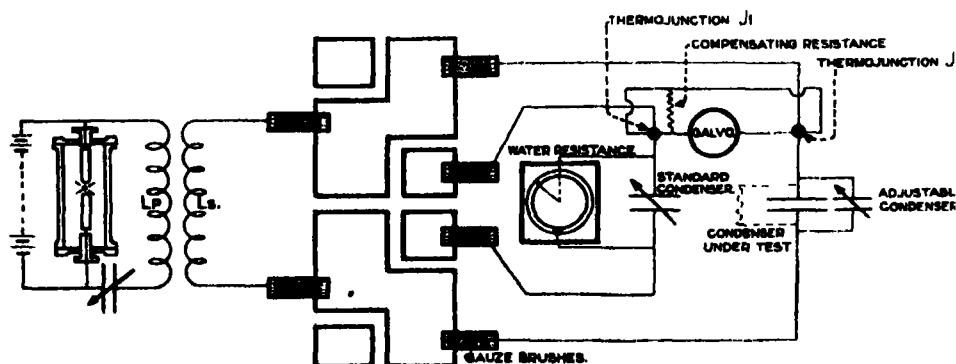


Fig 1. Shewing Commutator Circuits for High Frequency Measurements.

electric motor, alternately, and for equal times, inserts either of the two condensers in series with the inductance  $L_s$ , forming a secondary to the primary  $L_p$ . Two thermo-junctions,  $J_1$  and  $J_2$ , are arranged, one in each circuit, in such a manner that the E.M.F.'s produced by them oppose one

\* As this work was carried out in 1913-1914, three electrode valves of sufficient power were not available.

another. When the galvanometer placed in the circuit common to both gives no deflection, then we know that the two conditions mentioned above are fulfilled. This arrangement being a null reading one, makes it independent of any irregularities in the source of the oscillations. It also enables us to approach zero from either side, for it is apparent that, according as one conductance is greater or less than the other, so will its corresponding resonance current be less or greater than the other, and therefore for one E.M.F. to preponderate over the second.

For ease of construction, the commutator was built up of six brass rings, mounted on red fibre discs supported on a steel spindle. The two end rings as well as the two middle ones were split in half. One half of each split ring was electrically connected to the neighbouring whole ring in the manner shown in fig. 1. Six small gauze brushes lead the current from the various circuits, and in such a manner that once during each revolution of the commutator, and for equal times, each condenser is inserted in the resonating circuit.

The dielectrics were made up into small condensers with tinfoil interleaved between the sheets, each condenser having a capacity of from 300 to 2000 micro-micro-farads. The condenser under test being of a constant value, a series of inductances ranging from 0.005 to 0.1 millihenry were used, depending at what particular frequency measurements were being made.

The adjustable standard of resistance being very high, of the order of half a megohm, a wire resistance was quite out of the question, especially at high frequencies. A water resistance was therefore used. This consisted of a block of paraffin wax, in which a circular channel was cut, about 15 cm. in diameter, the area of channel about 1 sq. cm. A plug of wax was then made in the channel near one terminal (fixed); the other terminal consisted of a small thin plate of copper attached to a radial arm. This enabled one to obtain a continuous range of resistance from zero up to a maximum depending upon circumstances. Either distilled water or slightly acidulated water was poured into the channel, the maximum resistance depending upon the particular dielectric under test, and on the frequency used during the test. The highest resistance obtainable was about 2 megohms. The arrangement which was kept in a glass case was calibrated at the beginning and end of each day's work.

The thermo-junctions were of the type devised by Dr. J. A. Fleming. It is necessary that they should be both of exactly the same resistance in the heater wire, in order that the total resistance decrement of the two circuits should be the same, and what is more, the magnitude of the heater resistance should be as small as possible, consistent with sensitiveness, in order to cut

down the resistance decrement. It may be pointed out that if we are dealing with a constant E.M.F. induced in a resonating circuit having only resistance decrement, the deflection of a thermal ammeter is inversely proportional to the effective resistance of the circuit  $R$ . As the effective resistance of the inductance coil  $L_s$  was very small, we may take  $R$  as being equal to the resistance of the heater wire in the thermo-junction. Then if  $I$  be the resonance current, we have

$$I = E/R \text{ (when the circuit is tuned)}$$

$$\text{and heat developed} = RI^2,$$

$$\therefore \text{heat developed} \propto 1/R,$$

$$\therefore \text{galvanometer deflection} \propto 1/R.$$

Hence the smaller we make  $R$ , the greater will be the deflection. There are, however, two factors which limit the above.  $R$  cannot be made too small, for this means a thick wire and therefore a larger surface for radiation and a lower temperature of the thermo-junction. Again, a small  $R$  means a large voltage across the condenser, and this we decided must be kept low in order to prevent any possibility of brush discharge with the thin dielectrics used in making up the condensers.

In the above we have neglected the decrement of the condenser itself, but taking this into account, it would still remain true that the smaller  $R$  is the greater will be the galvanometer deflection. It therefore suggests that we should make the heater of the metal having the best electrical conductivity, viz., silver. The heaters finally used were 0.025 mm. diameter, and had a resistance of 0.23 ohm. So, at the highest frequency used,  $2 \times 10^6$ , and a capacity of 1000 micro-micro-farads, the power factor of the inductance and heater would be

$$= R/L_p = pCR = (2\pi \times 2 \times 10^6) \times 1000 \times 10^{-12} \times 0.23 = 0.0029.$$

The total power factor of the entire oscillating circuit, including the commutator, and apart from the condenser itself, was approximately twice this value, about 0.007. Since this is much less than the power factors of the condensers tested, it follows that the greater part of the decrement of the oscillating circuits resided in the condensers themselves, and the experiments were therefore conducted under the best possible conditions as regards the production of resonance.

The junctions gave with a Paul 10-ohm galvanometer a maximum deflection for 0.08 ampère. Under the above circumstances the E.M.F. on the condenser would be 8 volts. At the lowest frequencies, from half-a-million downwards, in order not to increase this voltage above about 10 volts, a second

pair of junctions were used, having each a resistance of about 0.95 ohm, giving a resistance decrement of approximately the same order of magnitude as before, because we should be using a proportionately larger inductance.

A second requirement of the thermojunctions is that they should be exactly equal as regards sensitiveness, *i.e.*, must give equal deflections on the galvanometer for equal currents in either. With a little manipulation of the soldered junction it is possible to get them so to within 4 or 5 per cent. The remaining difference can be compensated for by shunting the more sensitive one with a resistance until they give the same deflection (see fig. 1).

Although it is possible to obtain no reading on the galvanometer with the commutator running, and definite equal currents in each circuit, it does not follow that there will be a balance for all equal currents, either below or above. This necessarily follows from the impossibility of obtaining both the heating and radiation constants of the two thermo-junctions exactly similar at all temperatures. Fig. 2 shows how close we may get to perfect equality under all conditions. The abscissæ give the current in either of the thermo-

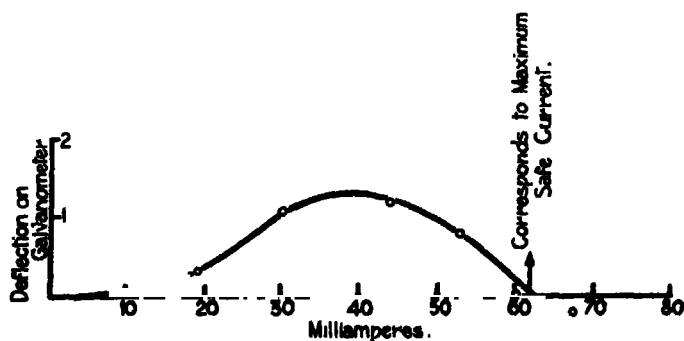


Fig 2. Shewing the Out-of-Balance Deflection on Commutator for Different Currents in the Thermo-junctions.

junctions, and the ordinates the out-of-balance deflection on the galvanometer. It will be seen that we have a zero deflection for 63 milliamperes, which was the maximum safe current in the junction in question. This corresponds to a galvanometer deflection of 100 divisions. At 40 milliamperes we have a maximum out-of-balance current of 1.3 divisions; this, however, is very small compared with the total deflection, and only introduces a possible error of between 1 and 2 per cent. The junctions could stand an overload current up to 80 milliamperes.

As the source of oscillations a graphite arc in air, shunted with inductance and capacity, was employed. Above about 200,000 ~ per second, it was

found impossible to obtain sufficient power in the secondary circuit without making the coupling too tight. Placing the arc in compressed air at about five atmospheres pressure enabled a much greater power to be taken out and increased the available frequency to about a million or so. Hydrogen was also tried as recommended by Poulson and others, but while the oscillations are stronger, they are much less steady, and, what is much more unsatisfactory, it gives a very impure wave, and the circuit is exceedingly difficult to tune, as the frequency varies with the arc current. The latter point has also been observed by L. W. Austin.\* The graphite arc in compressed air, on the other hand, for some reason which is not very plain, tends to suppress all the higher harmonic components of the main oscillations and gives a nearly pure sine wave.

The limit at which one can obtain steady oscillations with the Duddell arc is about 500,000 ~ per second. Beyond this the arc behaves very erratically and constantly fluctuates; at 2,000,000 ~ oscillations are only intermittent. The author has succeeded in obtaining fairly steady continuous oscillations up to about  $5 \times 10^6$  ~ per second by means of the arrangement of circuits shown in fig. 3. The circuit A is tuned to a frequency at which steady oscillations can be obtained, i.e., from 500,000 to  $10^6$ , and circuit B, placed so that it can

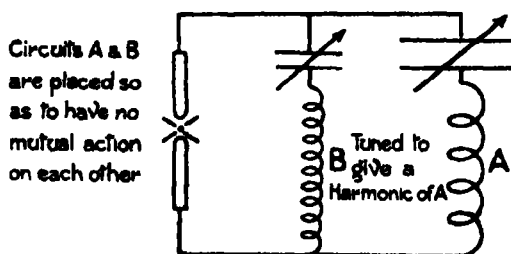


Fig 3. Scheme of Parallel Circuits to give Very High Frequency Currents.

have no mutual action on A, is tuned to a harmonic, either second, third fourth, or fifth of circuit B. Under these circumstances, oscillatory currents of these different frequencies can easily be obtained, circuit A acting with a steadying influence. If circuit A is tuned to a frequency of  $10^6$  and B to  $3 \times 10^6$ , and the oscillations started, it is found that if the lower frequency circuit A is cut out, the oscillations are immediately stopped in the higher frequency circuit B. On making circuit A again, the oscillations in B

\* 'Bull. Bureau Standards,' vol. 3, p. 325 (1907).



immediately restart. It was only by the use of this arrangement that it was possible to reach the extreme limit of  $3 \times 10^6 \sim$  per second, to which the observations were carried for the last three dielectrics mentioned below.

The actual method of procedure followed in making the measurements was as follows:—With the commutator at rest each condenser was adjusted for maximum resonance current. The commutator was then set running and the out-of-balance current flowing through the galvanometer was brought to zero by varying the resistance shunted across the standard air condenser. This adjustment in the case of the poorer dielectrics would need a slight alteration in capacity of the standard air condenser to bring the circuit into resonance again. A final readjustment of the shunted resistance would then bring the circuits into perfect equality.

If  $C$  and  $S$  be the capacity and conductance of the unknown condenser under test,  $C_s$  the capacity in parallel with it to produce resonance,  $C_e$  the capacity in the standard circuit to produce resonance, and  $R$  the shunted resistance, then

$$C = C_s - C_e \quad \text{and} \quad S = 1/R.$$

From  $C$  and  $S$  knowing the ratio of area to thickness for the dielectric we can calculate  $\sigma$  and  $K$  the specific alternate current conductivity, and the dielectric constant.

The frequency from 400,000  $\sim$  per second and upwards was measured with a Fleming cymometer. The lower range was determined with another made-up cymometer, consisting of a variable air condenser, reading from 200 and 3300 micro-micro-farads combined with a single layer solenoidal coil. The inductance of the latter was calculated by Russell's formula and found to be 0.238 millihenry; its measured value at telephonic frequencies by the Anderson bridge method was found to be equal to 0.233 millihenry. This value requires a slight correction when used at high frequencies. This correction was applied by Heaviside's formula:\*

$$L_0 - L_\infty = 0.026 \left( \frac{N^2 a d}{l} \right) \text{ microhenry,}$$

where  $N$  equals number of turns,  $a$  equals radius of coil,  $d$  equals diameter of wire and  $l$  equals the length of the coil. These quantities were respectively 66, 4.15, 0.091 and 7.9, and therefore gave a correction of 0.0055 millihenry. The value of the coupling inductance at high frequencies was therefore taken as being equal to 0.233—0.005 or 0.228 millihenry.

\* 'Electrical Papers,' vol. 1, p. 356.

### 3. Discussion of Experimental Results.

In the Tables are given the experimental results obtained for the following dielectrics :—Blotting paper, glass, guttapercha, vulcanised indiarubber, marble and slate. The general nature of the results is to show that the conductivity increases enormously as the frequency increases. The linear law found by Dr. Fleming and Mr. Dyke\* connecting the two quantities at telephonic frequencies is now no longer obeyed, but the conductivity gradually tends to a maximum and then seems to decrease again.

We will now discuss the behaviour of each particular dielectric in turn.

(a) *Blotting Paper*.—Table I gives the results for a condenser made up of good white blotting paper which had been previously dried in an oven. The first three columns give the values of the measured conductance  $S$  and capacity  $C$  at given frequencies. The last three columns give the values of the dielectric constant, specific conductivity, and  $S/Cp$  (approximately proportional to the power-factor) as calculated from these quantities  $S$  and  $C$ . The observations are depicted in fig. 4. It will be seen that the conductivity at first proportional to the frequency quickly rises to a maximum at about 600,000 ~ per second, and then decreases again. In the curve showing the variation of dielectric constant with frequency we have a sharp fall at

Table I.—Dielectric: Dried Blotting Paper. Area = 105 sq. cm.

Thickness = 0.042 cm.  $\frac{\text{Area}}{\text{thickness}} = 2480.$

Frequency, ~ per sec.	Capacity in micro- micro-farads C.	Conductance in micro-mhos S.	$S/Cp$ .	Dielectric constant.	Conductivity in micro- micro-mhos per cm. cube.
920	400	0.875	0.038 (0.0009)†	1.88	35.2
2,760	395	0.135	0.019 (0.0005)†	1.81	53
4,600	393	0.190	0.0165 (0.0105)†	1.80	76
180,000	375	8.25	0.019	1.72	3,320
210,000	380	10.4	0.021	1.74	4,200
235,000	377	16.6	0.030	1.72	6,700
255,500	375	19.5	0.029	1.72	7,900
320,000	375	23.0	0.030	1.72	9,350
360,000	375	25.5	0.030	1.72	10,300
445,000	375	50.5	0.048	1.72	20,200
495,000	373	62.5	0.054	1.71	25,200
580,000	370	68.5	0.051	1.69	27,400
780,000	350	52.5	0.0305	1.60	21,200
880,000	340	42.5	0.0195	1.55	17,100

† The numbers in the brackets are the values of the power-factor calculated by subtracting the ordinary direct current component from the total conductance.

\* 'Journ. Inst. Elec. Eng.,' vol. 49, p. 323 (1912).

telephonic frequencies and then a gradual decrease as the frequency increases. In drawing the  $S/Cp$  curve we have, for the telephonic range of frequencies,

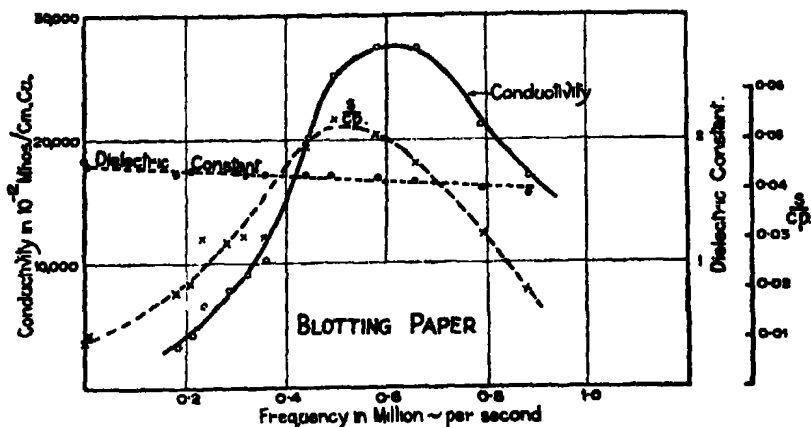


Fig 4 Variation with Frequency of the Conductivity,  $S/Cp$ , & Dielectric Constant of Blotting Paper

separated out the ordinary direct current component of the conductivity which is superposed on the true alternate current conductivity. Thus if  $S$  = total measured conductivity, and  $S_0$  = that due to the direct current component, then  $(S - S_0)/Cp$  represents the power-factor due to the alternate current conductivity alone. These values are given in the brackets in column 4. At the higher frequencies  $S_0$  is too small compared with  $S$  to have any influence on  $S/Cp$ . The result of these calculations is to give an intercept on the axis of conductivity indicating that from  $n = 0$  up to about  $n = 50,000$  ~ per second we have a constant power-factor (see fig. 4) approximately equal to 0.01. Above this there is an increase in the power-factor proportional to the frequency, that is to say,  $S/Cp$  may be represented as the sum of two quantities:—

$$S/Cp = x + yp,$$

or, what is the same thing, .

$$\sigma = an + bn^2.$$

It is apparent, therefore, that we are dealing with two separate effects, one implying a loss proportional to the frequency, and the other a loss proportional to the square of the frequency. At telephonic frequencies the first term is the only one of importance. At higher frequencies the second has the more influence. The first implies a loss which is independent of the time taken for taking the dielectric through a complete cycle, and we will, therefore, tentatively designate it a "dielectric hysteresis" loss.

The second which is a loss depending upon the time taken to complete the cycle will, for reasons to be given later, be called a "viscous" loss.

A comparison of the different quantities for low and for high frequencies is instructive. Thus, the maximum power-factor (0.054) is  $5\frac{1}{2}$  times as great as the power-factor at telephonic frequencies (0.01). The calculated value of the D.C. component is  $26.7 \times 10^{-12}$  mhos per cubic centimetre. Therefore the maximum conductivity at high frequencies is  $27,500/26.7$ , or 1020 times as great as the conductivity with steady currents.

(b) *Crown Glass*.—The condenser used for these experiments was the thin crown-glass used for the cover-glasses of microscope slides. The results are given in Table II and are plotted in fig. 5. The general nature of the curves is similar to that of the ones for blotting-paper. The linear part of the conductivity curve extends over a wider range, and the point of maximum conductivity is a little lower, viz., 510,000 ~ per second. The calculated value of the D.C. conductivity is  $12 \times 10^{-12}$ , and therefore the maximum alternating current conductivity is  $30,500/12$ , or 2500 times as large.

The  $S/C_p$  curve is slightly different. It will be seen that it has a relatively larger intercept on the axis of co-ordinates, implying that hysteresis contributes more to the conductivity than viscosity, for the maximum  $S/C_p$  (0.023) is only 50 per cent. greater than the constant  $S/C_p$  corresponding

Table II.—Dielectric: Crown-glass. Area = 55 sq. cm.

$$\text{Thickness} = 0.206 \text{ cm.} \quad \frac{\text{Area}}{\text{thickness}} = 2760.$$

Frequency, ~ per sec.	Capacity in micro- micro-farads C.	Conductance in micro-mhos S.	$S/C_p$	Dielectric constant.	Conductivity in micro- micro-mhos per cm. cube
920	1547	0.16	0.018 (0.0145)*	6.80	61
2,760	1535	0.435	0.017 (0.0155)*	6.56	164
4,600	1530	0.682	0.0145 (0.0145)*	6.53	256
150,000	1505	25.2	0.0175	6.40	9,450
180,000	1500	30.0	0.0176	6.35	11,200
230,000	1490	41.5	0.019	6.30	15,600
270,000	1475	58.0	0.023	6.25	21,800
295,000	1470	60.0	0.022	6.2	22,500
335,000	1470	68.0	0.022	6.2	25,500
395,000	1475	70.5	0.019	6.25	26,500
460,000	1470	81.5	0.019	6.2	30,500
510,000	1455	80.0	0.017	6.15	30,000
580,000	1470	74.5	0.014	6.2	28,000
620,000	1460	65.5	0.0115	6.15	24,500
705,000	1460	61.5	0.0095	6.15	23,000
800,000	1470	61.5	0.0085	6.2	23,000

\* The numbers in the brackets are the values of the power-factor calculated by subtracting the ordinary direct current component from the total conductance.

to low frequencies (0.015). The further course of the curve is interesting, for it eventually falls to a value only half that of the intercept for  $n = 0$ , and

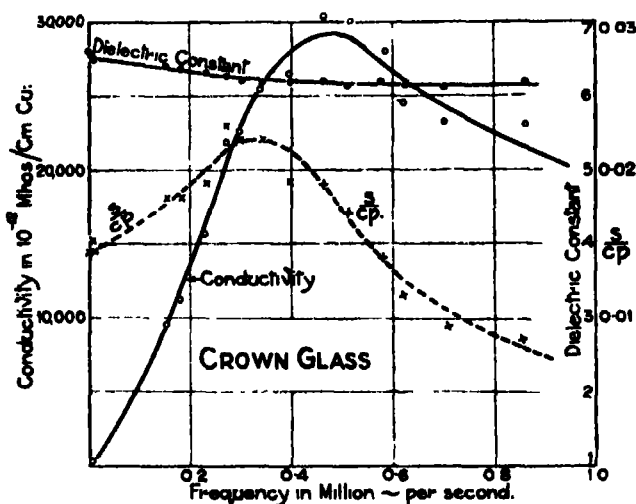


Fig 5 Variation with Frequency of the Conductivity,  $C_p$ , and Dielectric Constant of Crown Glass.

is still rapidly decreasing. This indicates that the hysteresis loss per cycle which is constant at low frequencies, decreases and tends to become zero at higher frequencies, viscosity only being of importance.

During the observations on glass, means were taken to see whether the alternate current conductivity varied with the voltage. This was done by balancing the commutator for some particular coupling of the primary and secondary and then altering it by either increasing or decreasing the distance between them. No alteration of the balance was required although the voltage conditions were such that at the lower limit only about 2 volts were across the condenser, and at the higher limit a perceptible noise inside the condenser indicated that brushing had just set in. This confirms for high frequencies what B. Monasch found at telephonic frequencies—the energy loss in a dielectric is strictly proportional to the square of the voltage, provided brush discharge is eliminated.\*

(c) *Vulcanised Indiarubber*.—This dielectric is one of the two (gutta-percha being the other) out of all those tested by Dr. Fleming and Mr. Dyke, whose conductivity they found was incapable of being represented within the telephonic range of frequency by the linear law

\* "Dielectric Losses," 'Ann. der Phys.,' vol. 22, p. 805 (1907); or 'Science Abstracts,' 10 B, No. 897 (1907).

$\sigma = a + bn$ ,  $\sigma$  increasing much more rapidly. This is illustrated by the first three rows of figures in Table III; the power-factor for  $n = 920$  is 0.002, whereas for  $n = 4600$  it is nearly twice as great, being 0.0035. The reason for this is clearly seen on inspection of fig. 6, for there we see that

Table III.—Dielectric: Vulcanised Indiarubber. Area = 55 sq. cm.

Thickness = 0.053 cm.  $\frac{\text{Area}}{\text{thickness}} = 1030$ .

Frequency, ~ per sec.	Capacity in micro- micro-farads C.	Conductance in micro mhos S.	S/Cp.	Dielectric constant	Conductivity in micro- micro-mhos per cm. cube.
920	240	0.003	0.002	2.73	3
2,760	247	0.012	0.0025	2.70	12
4,600	247	0.023	0.0035	2.70	22
210,000	245	8.2	0.025	2.68	7,900
235,000	243	9.50	0.027	2.65	9,100
305,000	243	16.3	0.035	2.65	15,900
325,000	245	18.8	0.038	2.68	18,200
360,000	245	17.4	0.032	2.68	17,000
375,000	240	15.9	0.028	2.62	15,500
395,000	240	16.1	0.027	2.62	15,700
405,000	230	18.2	0.031	2.51	17,600
430,000	235	26.3	0.0415	2.57	25,500
480,000	235	38.0	0.053	2.57	37,000
515,000	225	42.5	0.058	2.45	41,000
560,000	230	50.0	0.062	2.52	48,500
650,000	240	48.5	0.049	2.62	47,000
720,000	240	39.3	0.036	2.62	38,000
880,000	225	29.5	0.0235	2.45	28,800

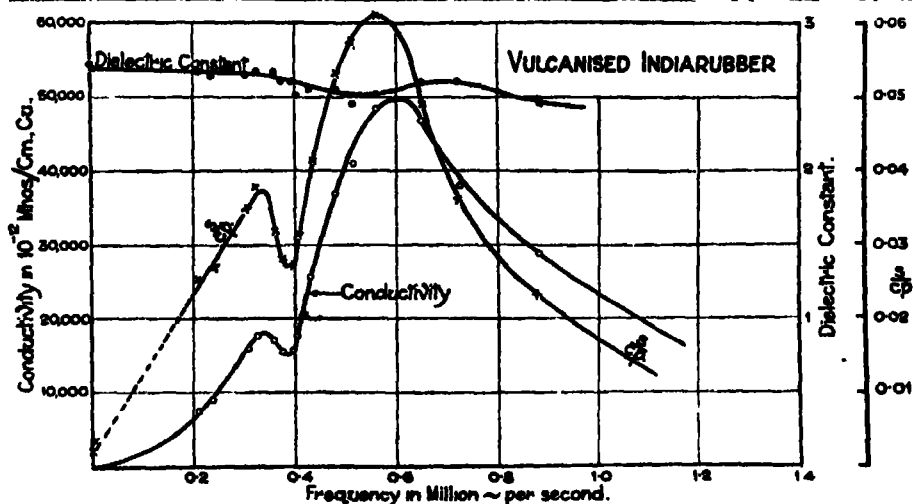


Fig 6. Variation With Frequency of the Conductivity,  $S/Cp$ .  
& Dielectric Constant of Vulcanised Indiarubber.

the intercept on the co-ordinate axis is very small, so that it is only over a very short range, say up to 400  $\sim$  or 500  $\sim$  per second, that  $S/C_p$  can be called even approximately constant (by interpolation being about 0.0015). The viscous loss is, in fact, of so much greater importance, that at 350,000  $\sim$  per second, the power-factor is 0.038, or 23 times as large as at very low frequencies. Hysteresis is therefore, comparatively speaking, absent.

For a very considerable range, from  $n = 0$  up to  $n = 350,000 \sim$  per second,  $S/C_p$  is exactly a linear function of the frequency, or

$$\sigma = bn^2.$$

The conductivity has a maximum value at about 560,000  $\sim$  per second, and increases so rapidly with frequency that it is 16,000 times as great as at  $n = 1000$ . There is also a subsidiary maximum at 350,000  $\sim$  per second, causing a slight hump on the curve, and indicating the existence of two components in the dielectric.

It remains now to point out a remarkable agreement between the maximum power-factor observed above on the power-factor-frequency curve and the maximum power-factor observed by Fleming and Dyke for vulcanised indiarubber at certain low temperatures. They found that at about  $-30^\circ \text{C}$ . the conductivity at a given frequency rose very rapidly and reached a maximum of considerable value, fourteen times that at ordinary temperatures. The power-factor at this point was 0.034, and was independent of the frequency. Now, the power-factor observed above for the first hump on the conductivity-frequency curve is 0.038, which agrees fairly well with the former figure. If we allow for the slight change of capacity with frequency and temperature, the agreement is still closer.

(d) *Guttapercha*.—This dielectric is another material that does not follow a linear law in the variation of conductivity with frequency within the telephonic range. In the last case (vulcanised indiarubber), it was due to the fact that the hysteresis loss was negligible in comparison with the viscous loss. In the case of guttapercha, however, the divergency results from quite a different cause, being due to the presence of a component in the dielectric having a frequency of maximum conductivity which is only just outside the telephonic range. Thus, if we inspect Table IV, we see that the power-factor increases from 0.014 at  $n = 920 \sim$  per second up to 0.027 at 15,000  $\sim$  per second. This was the upper limit imposed by the limits of audition on measurements made with the bridge and telephone. At  $n = 210,000 \text{ S/C}_p$ , however, has fallen to 0.019, implying the existence of a slight hump on the conductivity-frequency curve at 50,000  $\sim$  per second. It was not possible to make any measurements at lower frequencies, because with the present experimental arrangements they would entail a considerable

Table IV.—Dielectric : Guttapercha. Area = 110 sq. cm.

$$\text{Thickness} = 0.0582 \text{ cm.} \quad \frac{\text{Area}}{\text{thickness}} = 1890.$$

Frequency, ~ per sec.	Capacity in micro- micro-farads C.	Conductance in micro-mhos S.	S/Cp.	Dielectric constant.	Conductivity in micro- micro-mhos per cm. cube.
920	485	0.38	0.014	2.92	20
2,760	479	0.158	0.019	2.88	84
4,800	475	0.305	0.022	2.85	180
15,000	470	0.79	0.027	2.82	416
180,000	460	11.2	0.019	2.76	5,900
235,000	460	11.8	0.018	2.70	6,250
250,000	455	13.4	0.018	2.73	7,100
295,000	455	15.0	0.018	2.73	7,950
320,000	460	17.9	0.019	2.76	9,500
365,000	455	19.6	0.0195	2.73	10,300
400,000	453	22.3	0.020	2.72	11,800
410,000	450	23.4	0.021	2.70	12,400
445,000	453	29.1	0.021	2.72	15,400
555,000	450	45.3	0.028	2.70	24,000
600,000	450	61.4	0.036	2.70	32,500
660,000	450	70	0.036	2.70	37,000
1,000,000	445	52	0.019	2.67	27,500
1,040,000	440	47	0.0165	2.64	24,800
1,350,000	440	39.5	0.0105	2.04	20,800
1,700,000	435	27.8	0.006	2.62	14,700

voltage on the condenser to obtain sufficient current. For this reason, the curve has had to be filled in tentatively by means of the dotted line. From about 300,000 ~ per second and upwards, the conductivity and S/Cp curves (see fig. 7) are precisely similar to those of the dielectrics already considered,

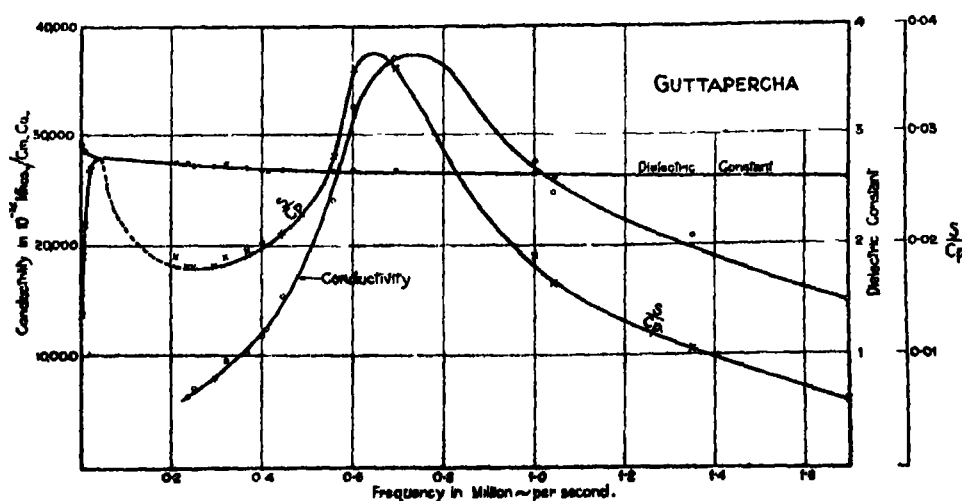


Fig 7. Variation with Frequency of the Conductivity,  $S/C_p$ , & Dielectric Constant of Guttapercha.



in that they rapidly rise up to a maximum and decrease again; the frequency for maximum conductivity in this case is about 750,000  $\sim$  per second.

By interpolation the power-factor for very low frequencies ( $n = 0$ ) is 0.011, and it will be seen that if we prolong the base of the second hump of the  $S/Cp$  curve backwards in a straight line it will also cut the vertical axis at a point very close to this. In other words, each of the two components in the dielectrics, except for frequencies in the neighbourhood of its own peak, has little influence on the conductivity at other parts of the curve, both commencing with a common  $S/Cp$  arising from hysteresis.

As in the previous case the maximum power-factor observed at the first hump on the power-factor curve agrees approximately with the maximum power-factor observed at telephonic frequencies by Fleming and Dyke at a certain low temperature (8° C.). They found a maximum power-factor at this temperature, which was *independent* of frequency and amounted to 0.025. The maximum power-factor observed above on the conductivity-frequency curve at ordinary temperatures is 0.028. This coincidence is very striking and may be of interest in developing the theory of dielectrics under alternating E.M.Fs.

(e) *Marble*.—The next two dielectrics to be considered are typical constituents of the earth's crust. In the case of marble the curves present some points of difference from those already considered. The experimental results are given in Table V and depicted in fig. 8. They refer to a condenser made up of 20 square marble slabs\* about 0.7 cm. thick, and effective area coated with tinfoil of 2400 sq. cm. Only 16 were effective, the remaining 4 being used on the outside of the condenser to carry the lines of force from the outside faces of the last tinfoil electrode. The whole was bolted together with two bolts.

As with the other dielectrics, the dielectric constant at first falls rapidly within the telephonic range, and then slowly decreases as the frequency reaches those used in radiotelegraphy. The conductivity-frequency curve however is different, in that after the usual linear stage at the beginning, the curve in approaching its maximum gradually bends over, instead of turning upward. The result of this is that the power-factor throughout the whole range decreases with increase of frequency.

At the very highest frequencies it may be noticed that, as regards power-factor, marble is better than any of the other dielectrics, the lowest  $S/Cp$  reached being 0.0033.

The calculated value of the D.C. conductivity is  $310 \times 10^{-12}$  mhos per

\* I have to express my indebtedness to Dr. J. A. Fleming, F.R.S., for placing these marble slabs at my disposal.

cubic centimetre, while the maximum A.C. conductivity is 23,000, the ratio being 74.

Table V.—Dielectric: Marble. Area = 2400 sq. cm.

Mean thickness = 0.67 cm.  $\frac{\text{Area}}{\text{thickness}} = 3500$ .

Frequency, ~ per sec.	Capacity in micro- micro-farads C.	Conductance in micro-mhos S.	S/Cp.	Dielectric constant.	Conductivity in micro- micro-mhos per cm. cube.
920	2771	1.48	0.093 (0.025)*	8.88	425
2,760	2707	2.12	0.047 (0.024)*	8.75	627
4,600	2675	2.58	0.035 (0.021)*	8.55	768
44,000	2570	18.7	0.019	8.40	3,950
155,000	2545	33	0.0135	8.20	9,500
235,000	2500	40	0.011	8.05	11,500
285,000	2510	54	0.012	8.1	15,500
320,000	2510	56	0.011	8.1	16,000
390,000	2500	59.5	0.0095	8.05	17,000
450,000	2440	63	0.0088	7.85	18,000
610,000	2440	57	0.006	7.85	20,000
740,000	2440	60	0.0053	7.8	21,000
980,000	2405	63	0.0045	7.75	22,000
1,050,000	2320	63	0.0041	7.50	22,000
1,170,000	2300	61.5	0.0036	7.40	21,500
1,400,000	2265	65.5	0.0033	7.30	23,000

\* The numbers in the brackets are the values of the power-factor calculated by subtracting the ordinary direct current component from the total conductance.

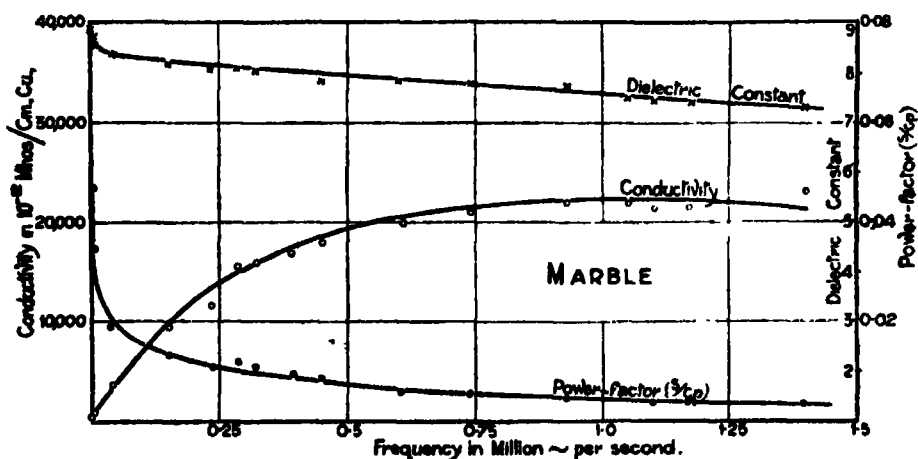


Fig 8. Variation With Frequency of the Conductivity,  $\frac{S}{Cp}$ , & Dielectric Constant of Marble.

(f) *Slate*.—The results for the slate condenser are given in Table VI and depicted in fig. 9. The frequency was taken up to 3,000,000 cycles per

second, and it will be seen that the conductivity is still rising, although there seems to be a tendency for the curve to flatten and turn over again. At the same time there are several irregularities on the curve, which seem to indicate that there are several component materials in the slate. The most noticeable point about the dielectric constant curve is its enormous drop at low frequencies, K being about 50 at  $n = 920$ , whereas at 500,000  $\sim$  per second, it has fallen to about 10.

This large drop in K causes the power-factor to be approximately constant over a wide range of frequency, whereas if we calculate  $(\sigma - \sigma_0)/n$ , which is proportional to the amount of work done per cycle due to the alternating conductivity, it will be seen that this quantity after being approximately

Table VI.—Dielectric: Slate. Area = 55.8 sq. cm.

$$\text{Thickness} = 0.162 \text{ cm.} \quad \frac{\text{Area}}{\text{thickness}} = 344.$$

Frequency, $\sim$ per sec.	Capacity in micro-micro- farads C.	Conductance in micro- mhos S.	S/Cp.	$(\sigma - \sigma_0)/n$ $\times 10^6$	Dielectric constant.	Conductivity in micro- mhos per cm. cube $\sigma$ .
920	1520	3.00	0.342	7.8	50.0	0.00872
2,760	1255	8.05	0.369	7.9	41.5	0.0233
4,800	1145	13.3	0.400	8.0	37.5	0.0386
12,000	850	29.5	0.455	7.2	28.0	0.086
44,000	620	69	0.405	5.95	20.5	0.20
110,000	500	115	0.33	3.1	16.5	0.34
230,000	450	190	0.29	2.4	14.8	0.55
300,000	390	250	0.34	2.4	12.8	0.73
410,000	390	292	0.295	2.05	12.9	0.85
520,000	350	355	0.255	2.0	11.5	1.03
620,000	315	400	0.250	1.85	10.8	1.15
700,000	320	415	0.245	1.7	10.5	1.20
780,000	325	455	0.23	1.7	10.6	1.33
820,000	325	480	0.23	1.7	10.6	1.40
880,000	330	500	0.27	1.65	10.3	1.45
940,000	340	525	0.26	1.65	11.3	1.53
980,000	320	525	0.265	1.6	10.6	1.53
1,020,000	310	530	0.265	1.5	10.3	1.54
1,050,000	340	525	0.25	1.45	11.2	1.53
1,160,000	285	595	0.23	1.5	9.3	1.72
1,190,000	290	630	0.29	1.5	9.6	1.83
1,240,000	275	625	0.245	1.45	9.15	1.82
1,340,000	305	665	0.23	1.45	10.1	1.94
1,390,000	305	640	0.24	1.35	10.1	1.86
1,450,000	305	650	0.235	1.3	10.1	1.89
1,520,000	290	685	0.24	1.35	9.5	1.93
1,650,000	275	725	0.25	1.3	9.10	2.11
1,760,000	270	770	0.26	1.3	8.95	2.25
1,850,000	270	810	0.255	1.25	8.95	2.36
1,900,000	270	840	0.26	1.3	8.95	2.45
2,170,000	275	860	0.26	1.15	9.1	2.5
2,650,000	270	860	0.19	0.95	8.95	2.5

constant within the telephonic range decreases with increase of frequency from about  $7.8 \times 10^{-12}$  mhos per cycle per second to about  $1 \times 10^{-12}$ .

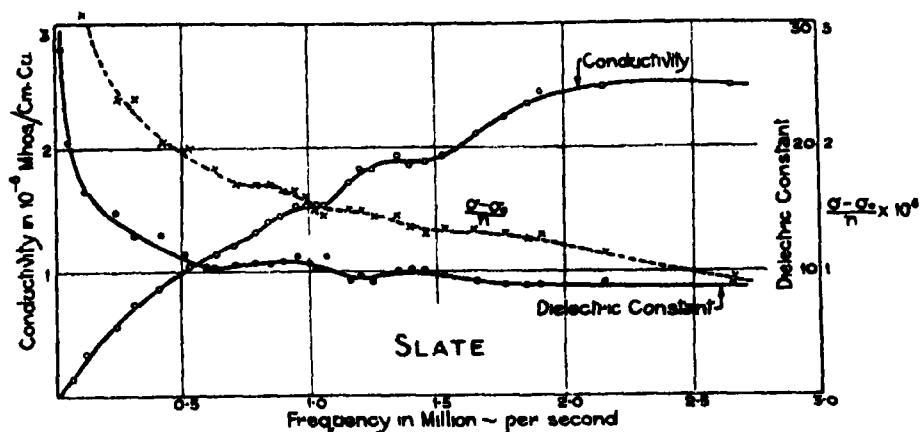


Fig 9. Variation with Frequency of the Conductivity,  $\frac{\sigma - \sigma_0}{n}$ , and Dielectric Constant of Slate

The maximum A.C. conductivity is  $2.5 \times 10^{-6}$  mhos per cubic centimetre, and the calculated value of the D.C. conductivity is 0.0015, hence the ratio of the two quantities is 1700.

#### Summary.

1. Measurements of the conductivity and dielectric constants of dry blotting paper, glass, vulcanised indiarubber, guttapercha, marble, and slate are given for alternating currents of low voltage and sine wave form, and for a wide range of high frequencies.

2. It is shown in all cases that there are present two independent sources of loss. One, a hysteresis loss, is usually the only one that is important at telephonic frequencies. The second, a viscous loss, has more influence at higher frequencies. The first loss is one which is independent of the time taken for a complete cycle, while the second depends upon this time and at low frequencies gives rise to a loss which varies as the square of the frequency.

3. The linear law found at telephonic frequencies connecting  $\sigma$  with frequency, is no longer obeyed at high frequencies, but  $\sigma$  gradually rises to a maximum, and then decreases again. This rise to a maximum is very rapid for some substances, *e.g.*, guttapercha and vulcanised indiarubber, while with slate and marble, the maximum is approached by the curve bending over instead of turning up. This leads to a very flat curve for which  $\sigma$  is practically constant over a considerable range of frequency.

4. The maximum A.C. conductivity is very much greater than the D.C.

conductivity. In the case of glass, it is 2500 times as large, while in the case of vulcanised indiarubber, the maximum A.C. value is even 16,000 times as large as the A.C. value at  $n = 1000$  — per second.

5. The constant hysteresis loss per cycle at low frequencies tends to become zero at very high frequencies.

6. The dielectric constant after a rapid drop at low frequencies, slowly decreases as the frequency rises.

In conclusion, I wish to express my indebtedness to Dr. J. A. Fleming, F.R.S., for placing the resources of his laboratory at my disposal, and for much valuable advice during the course of the work which was carried out during the years 1913 and 1914.

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### *On the Secondary Spectrum of Hydrogen.*

By T. R. MERTON, M.A., D.Sc.

(Communicated by Prof. A. Fowler, F.R.S. Received August 15, 1919.)

[PLATES 6 AND 7.]

Theoretical investigations of the origin of spectra in relation to the structure of the atom have concentrated especially on the spectrum of hydrogen, on account of the supposed simplicity of the hydrogen atom. They have, however, been confined almost exclusively to the Balmer series, and have ignored the difficulties which arise from the fact that hydrogen possesses another spectrum, usually known as the secondary spectrum, which is of great complexity, and the co-ordination of whose lines into recognised bands or series of lines is still in a very unfinished state. The investigations of Buisson and Fabry,\* in which the physical widths of spectrum lines were measured with the interferometer, refer at least a part of the lines of the secondary spectrum to the hydrogen atom, and the complications introduced into theoretical investigations cannot therefore be impartially waived by the assumption that the molecule is concerned in the production of the secondary spectrum.

As regards the relation of the two spectra, there is abundant evidence of a fundamental difference in their origin. In many celestial spectra the lines of the Balmer series constitute one of the most prominent features, whilst the identification of lines of the secondary spectrum is at least extremely

\* 'Journal de Physique,' vol. 2, p. 442 (1912).

doubtful. In the laboratory it has long been known that the relative intensity of the secondary spectrum is greatly reduced by the presence of impurities, notably oxygen, in vacuum tubes containing hydrogen, and by the passage of powerful condensed discharges. On the other hand, under conditions in which an uncondensed discharge from an induction coil is passed through very dry and pure hydrogen at a reduced pressure, the lines of the secondary spectrum may rival those of the Balmer series in intensity.

It would appear that little progress is to be looked for in the co-ordination into series of the lines of a spectrum of such complexity without recourse to physical methods which are capable of showing that certain lines or groups of lines are related, by the fact that their relative intensities alter in the same way, or that they vary in the same way in some other respect, under different physical conditions of excitation. Dufour,\* has shown that many of the lines can be separated into the categories of those which do and those which do not show the Zeeman effect, but a complete segregation of the spectrum into two classes by this method would seem to be very difficult, owing to the intrinsic faintness of many of the lines, which must of course be examined under a high dispersion in experiments of this kind. Dufour has also pointed out that the frequency differences of some of the weak lines are constant.

We owe an important advance in the elucidation of the spectrum to Fulcher,† who has shown that in low potential discharges the lines of the Balmer series become weaker, and that certain lines of the secondary spectrum can be seen to stand out very prominently under these conditions, whilst others are very faint, in comparison with their relative intensities, when the spectrum is examined of vacuum tubes excited by the uncondensed discharge from an induction coil. Fulcher showed that the differences in wave-length between many lines in the red and yellow regions were constant, and that they could thus be arranged into groups resembling bands, these "band" lines being the lines which were relatively enhanced in the spectrum of the low potential discharge spectrum, whilst (with two possible exceptions) the lines which were weaker in the low potential spectrum belonged to the class for which Dufour (*loc. cit.*) had observed the Zeeman effect. Measurements of the wave-lengths of the lines of the secondary spectrum have been made by Watson,‡ Hasselberg,§ Porlezza, and Porlezza and Norzi.|| A number of other observers have given measurements of a few of the lines.

\* 'Annal. Chim. Phys.' [3], vol. 9, p. 416 (1906).

† 'Astrophys. Journ.', vol. 37, p. 60 (1913).

‡ 'Roy. Soc. Proc., A', vol. 82, p. 189 (1909).

§ 'Mem. Acad. St. Petersb.' [7], vol. 31, No. 14 (1883).

|| 'Atti R. Accad. Lincei,' vol. 20 [2], p. 178 (1911), and vol. 20 [1], p. 822 (1911).

The marked variations in the intensities given by different observers, which seem in many cases quite outside the range of personal error, at once suggest that the relative intensities vary in a manner which is controlled by physical conditions which have not been precisely specified. As an example, Frost\* has measured the wave-lengths of a number of the stronger lines between  $\lambda = 4723$  A. and  $\lambda = 4358$  A. in the spectrum given by tubes containing a mixture of helium and hydrogen, and the intensities which he gives differ very conspicuously from those given by other observers.

It was intended to make an attempt to resolve the spectrum into groups of lines which showed a similar behaviour under different physical conditions, by investigating in the first instance the changes in the relative intensities of the lines which accompany a change of pressure in the discharge tube, the intensities being measured by means of the wedge method, which has been described in previous communications,† and a number of experiments have been conducted on these lines. The pressure in the vacuum tubes which were used was controlled by means of a short length of palladium tube, closed at one end and welded at the other to a platinum tube, the open end of which was sealed into a glass tube connected to the vacuum tube. The pressure of pure hydrogen in the vacuum tube could be raised, without introducing any impurities, by heating the palladium tube either in a current of hydrogen or in the centre of a flame of burning hydrogen, or lowered until the walls of the vacuum tube showed a bright green fluorescence, by heating the palladium in the highest point of the flame of a Bunsen burner, where the partial pressure of hydrogen is very low.

The results were promising in many respects, since they showed that the Fulcher bands become relatively brighter at low pressures, and at the same time there is a marked enhancement of the lines in the region of about  $\lambda = 5700$  A. to  $\lambda = 5000$  A. In the more refrangible region there is no conspicuous change in the relative intensities, but the intensity of the continuous spectrum is reduced at low pressures. It is probably on account of this continuous spectrum, which seems to increase in intensity in a regular manner towards the more refrangible region of the spectrum, that the difference in the spectrum at high and low pressures appears rather striking when the spectra are examined visually under a low dispersion; but the spectrograph which was available for measurements made in this manner was of somewhat too low a dispersion to afford the prospect, in view of the complexity of the spectrum, of a very complete segregation of the lines into different classes, though there is no doubt that results of some value would

\* 'Astrophys. Journ.,' vol. 116, p. 100 (1902).

† *E.g.*, Merton and Nicholson, 'Phil. Trans.,' A, vol. 217, p. 237 (1917).

be obtained with a spectrograph which was better suited to the investigation. This line of attack has been for the present postponed, owing to the discovery of a more potent method of altering the physical conditions by which the secondary spectrum can at once be sharply segregated into definite groups of lines.

It has been found that when hydrogen at a partial pressure of less than a millimetre is present in helium in vacuum tubes filled at a pressure of about 40 mm., the spectrum is remarkably different from that of pure hydrogen. As seen visually under a small dispersion, the effect is not very striking, but an examination with higher resolving power shows that the changes are of a fundamental character. The spectra have been photographed in the first order of a concave grating of 4 feet radius of curvature and ruled with 20,000 lines to the inch, which was mounted according to Eagle's method, the dispersion on the plate being almost exactly 10 Å. per millimetre.

With this instrument, photographs in juxtaposition were taken of the spectrum of a high-pressure helium-hydrogen tube and of a tube containing pure hydrogen at a pressure of a few millimetres, which was filled and regulated in the manner described above. The tubes were excited by the uncondensed discharge of an induction coil. In the more refrangible parts of the spectrum there is little difference, but in the red and yellow regions it is found that a large number of lines are greatly enhanced in the tubes containing helium, some of these being extremely faint in the spectrum of pure hydrogen, and that a number of new lines appear. There is another class of lines whose relative intensities are unaffected by the presence of helium, whilst a third class are affected in the sense that they become very weak or disappear. Small changes of intensity under different physical conditions would not constitute a safe criterion for the segregation of lines into classes, for it is known\* that lines belonging to the same series may undergo changes in their relative intensities under different conditions of excitation, but the changes which occur in the secondary spectrum of hydrogen, as a result of the presence of a large quantity of helium, are of a magnitude which leaves little room for doubt that a separation of the lines into physically related groups has been effected.

It has been mentioned above that the spectrum of a mixture of hydrogen and helium has been examined by Frost (*loc. cit.*), but his observations were confined to regions of the spectrum where the changes which occur are very slight, and it is likely that the pressure in his tubes was too low to show the phenomena. There seems little doubt that the new lines observed are to be assigned to hydrogen. They certainly do not occur in the spectrum of pure

\* Cf. Merton and Nicholson, *loc. cit.*



helium, and nearly all of the strongest lines from the high-pressure helium-hydrogen tubes are visible in pure hydrogen. Of the lines which are especially characteristic of these tubes, it is only (with a few exceptions) some of the weaker ones which are not seen at all in the spectrum of pure hydrogen.

There is naturally some ambiguity as to the correct exposures to be given for the purpose of dividing up the lines, but a plate in which the line  $H\alpha$  of the Balmer series appears somewhat more strongly in the spectrum of the helium-hydrogen tube seems to exhibit the phenomena very favourably, and this plate has accordingly been selected for the estimation of intensities. An examination of the spectrum of hydrogen reveals the fact that with long exposures a large number of lines, hitherto unrecorded, can be seen on the plate. Long exposures of the spectrum of the mixture of helium and hydrogen also show an immense number of faint lines. This is only to be expected in a spectrum which may be supposed to consist (at least in part) of bands, but it does not appear likely that the measurement of these very faint lines will be of much assistance at present in the elucidation of the structure of the spectrum. It is believed that the results can best be seen in the reproduction (Plates 6 and 7), in which the two spectra are shown in juxtaposition, with a wave-length scale adjoining the spectrum of hydrogen; the wave-lengths can be read with sufficient accuracy for identification in Watson's (*loc. cit.*) Tables. The principal helium lines are, of course, visible in the spectrum of the mixture.

It will be seen that the most conspicuous changes occur in the less refrangible regions. In the green and the more refrangible parts of the spectrum all the lines are greatly reduced in intensity in the spectrum of the mixture, but apart from this, and a few lines which seem abnormally weak, there is no conspicuous difference. The subjoined Table gives a list of lines which are either enhanced or unaffected in intensity by the admixture of the helium. These have been measured, using Watson's lines as standards, and it is believed that on his scale the values given are correct to a few hundredths of an Angstrom. All lines not recorded in the Table are weaker in the helium-hydrogen mixture. My own measurements of the few of these lines which occur in Watson's list are given; they have been derived from an error curve drawn through the readings of a number of lines measured by Watson and, excepting a few lines for which he found very low intensities, the results are in close agreement; 0 indicates that a line is just visible, and — that it is absent; a ? is added in cases in which it is doubtful whether the line in the helium-hydrogen mixture corresponds with a line in the spectrum of pure hydrogen.

5,400

6,000

5,500

6,100

5,600

6,200

5,700

6,300

5,800

6,400

5,900

6,500



4,300

4,900

4,400

5,000

4,500

5,100

4,600

5,200

4,700

5,300

4,800

5,400



List of Lines which are strengthened or unaffected in the presence of Helium.

$\lambda$ .	Intensity in pure hydrogen.	Intensity in hydrogen and helium.	$\lambda$ .	Intensity in pure hydrogen.	Intensity in hydrogen and helium
6406.02	0	1	5887.56	—	0
6412.01	1	1	5881.75	—	2
6893.26	—	1	5868.45	—	2
6818.92	1	3	5857.96	4	2
6287.21	—	0	5851.98	2	2
6276.89	—	1	5849.54	4	8
6260.83	—	1	5847.49	0	5
6246.98	2	2	5839.37	P	1
6234.14	2	4	5838.05	P	1
6194.03	<0	0	5831.26	2	7
6186.74	—	1	5829.00	—	0
6181.74	—	1	5824.78	1	3
6161.82	6	8	5819.60	2	8
6159.73	2P	2	5815.27	P	5
6141.12	—	4	5812.84	0	10
6119.19	3	3	5811.72	1	5
6112.98	—	1	5804.96	2	4
6111.29	—	1	5801.84	2	4
6089.97	0	4	5799.15	3	3
6085.48	—	5	5794.34	3	8
6072.21	P	2	5791.97	4	8
6066.62	3	3	5788.47	2	3
6064.50	—	3	5788.18	1	2
6066.83	1	5	5779.17	3	6
6045.59	1	3	5772.82	—	2
6042.90	1	4	5766.08	P	7
6033.16	10	12	5760.59	2	2
6023.97	6	8	5756.73	—	3
6018.54	10	10	5755.81	1	2
6007.05	2	5	5754.83	—	0
6003.07	7	9	5732.12	7	7
5998.23	1	2	5728.72	7	7
5994.29	5	5	5723.59	2	2
5987.52	—	0	5716.17	1	2
5982.82	8	10	5708.86	2P	7
5975.68	10	10	5700.84	1	4
5974.39	3	3	5697.61	1	4
5971.16	0	1	5692.64	—	2
5963.71	5	7	5689.43	8	8
5960.89	7	8	5684.28	2	4
5958.53	1	1	5682.67	1	4
5947.55	5	6	5676.33	—	1
5938.88	8	10	5674.26	—	1
5936.26	3	3	5672.95	0	3
5931.63	8	10	5667.54	0	3
5929.70	—	0	5659.63	0	3
5920.99	7	8	5657.99	0	1
5916.34	7	8	5653.73	0	1
5900.71	2	3	5647.59	—	0
5896.14	5	5	5642.88	3	3
5894.25	4	4	5637.65	0	2
5890.19	5	5	5572.68	—	1
5889.23	2	2	5560.29	—	0

from changes of temperature; however perfectly the plates have been worked and adjusted, there is always a small change in the diameters of the rings when the beam of light traverses different portions of the *etalon*. This change is too small to be noticed visually when the plates have been carefully adjusted, but is at once apparent when the photographs of the fringes are measured with the micrometer. A slight shift of the source of light, or a wandering of the arc while it is burning, causes in this way a very small but measurable dilatation or contraction of the fringes. This source of error can be overcome to a great extent by reducing the aperture of the *etalon*, which, however, introduces certain practical difficulties, and a different method has been adopted by which this source of error and that due to changes in temperature are automatically eliminated.

The procedure adopted has been to make an alloy of each of the metals to be examined with a suitable proportion of cadmium, and to reduce all observations to a selected fringe of cadmium as a standard. The cadmium fringes thus indicate any change of path difference, whether due to temperature or shift, and the correction to be applied to other lines can be easily and accurately determined. The cadmium green line  $\lambda = 5086 \text{ \AA}$ . has been used as a standard, and the line  $\lambda = 4800 \text{ \AA}$ . for a purpose which will be explained later. The complexity of these lines is of no consequence, since the settings of the micrometer are made on the "optical centre of gravity" of the fringes, and the same remark applies to the lead line  $\lambda = 4058 \text{ \AA}$ ., which is not only encumbered by a faint satellite, but which might be also affected by overlapping with a neighbouring line, though in this particular case both the satellite and the neighbouring line are of such a small intensity in comparison with the main line that their effect would scarcely be felt.

The optical difference of path of the *etalon* is 18.60 mm. (the knowledge of its value with greater precision can easily be shown to be irrelevant), and the difference in wave-length,  $\epsilon$ , corresponding to a shift of a whole fringe, is given by  $\epsilon = \lambda^2/D$ , where  $\lambda$  is the wave-length and  $D$  the optical difference of path. Thus, for the lead line  $\lambda = 4058 \text{ \AA}$ .,  $\epsilon = 0.084 \text{ \AA}$ ., and for the thallium line  $\lambda = 5350 \text{ \AA}$ .,  $\epsilon = 0.146 \text{ \AA}$ .

Since grating measurements have already shown that any differences of wave-length are less than this amount, it is evident that any difference in wave-length will be represented by a fraction of a fringe. Let  $n_1$  be the order of the innermost fringe of the cadmium line  $\lambda = 5086 \text{ \AA}$ . and  $n_4$  the order of the fourth ring counting from the centre, and let  $r_1$  and  $r_4$  be the radii of the rings respectively, and let the order of interference at the centre of the system be  $n_1 + \eta$ . Then, since the angular diameter of the fringes is

small,  $\eta = 3r_1^2/(r_1^2 - r_2^2)$ . Thus, the order at the centre of the system for Cd  $\lambda = 5086$  A. is  $n_1 + \eta$ , and in a similar way for, say, Pb  $\lambda = 4058$  A., the order is  $m_1 + \zeta$ , both these values being determined from measurements made on the same photograph, on which both sets of fringes are recorded simultaneously.

Owing to changes of temperature or shifting of the apparatus a second exposure may give different values. If on the second exposure the value for Cd  $\lambda = 5086$  A. is  $n_1 + \eta + \delta\eta$  it is evident that the corresponding value for Pb  $\lambda = 4058$  A. should be  $m_1 + \zeta + \delta\eta (5086/4058)$ . It is found most convenient in calculating the results to reduce all the values for Pb  $\lambda = 4058$  A. to a definite order for Cd  $\lambda = 5086$  A., say  $n_1 + 1$ . To effect this when the order at the centre of the system for Cd  $\lambda = 5086$  A. is  $n_1 + \eta$  the amount to be added to the measured value for Pb  $\lambda = 4058$  A. is  $5086 (1 - \eta)/4058$ , and when the measured value for Cd  $\lambda = 5086$  A. is  $n_1 + \eta + \delta\eta$  the correction becomes  $5086 (1 - \eta - \delta\eta)/4058$ . Measurements of different plates are thus reduced to the same standard.

If  $m_1 + \alpha$  is the value reduced to the standard for  $\lambda = 4058$  A. for one variety of lead, and  $m_1 + \alpha_1$  the corresponding value for lead from another source, the difference in wave-length will be  $e(\alpha - \alpha_1)$ . Measurements of the fringes of another cadmium line  $\lambda = 4800$  A. serve to identify the fringe  $n_1$  for the line  $\lambda = 5086$  A. A readjustment of the plates of the *etalon* might result in the innermost fringe being of the order  $n \pm 1$  or  $n \pm 2$ . If this change occurs it can at once be detected, since it follows from the preceding argument that the fractional values of the order for  $\lambda = 4800$  A. will not agree unless they have been reduced to the same standard.

Six plates have been taken of each alloy and the fractional part of the order at the centre has been determined from the mean of four measurements of the radii of the rings on each plate. The mean of the six values has been adopted, and the mean error calculated in the usual way.

*Ordinary Lead.*—A pure sample of ordinary lead was melted with  $4\frac{1}{2}$  times its weight of cadmium, and cast into sticks in holes in a wooden block.

*Lead from Radium.*—This was made into an alloy with cadmium in the same way. The lead had been extracted from Joachimsthal pitchblende residues, and although no special precautions were taken, spectroscopic examination showed that it was comparatively pure.

*Lead from Thorium.*—For this I am indebted to Prof. Soddy. On informing him of the results which had been obtained in the case of the lead and thallium from pitchblende, he at once very kindly sent me a pure sample of lead which he had extracted from Ceylon thorite, a mineral which contains



a large proportion of thorium, and only a very small quantity of uranium (about 2 per cent).

*Ordinary Thallium.*—A very small quantity of this element was dissolved in a few grammes of molten cadmium.

Thallium from pitchblende residues was not isolated. It was present in much too small a proportion for any attempt to do so with the amount of residues available.

It is unnecessary to give the details of the separation of a mixture of sulphides, which, when reduced and alloyed with cadmium, showed the thallium line  $\lambda = 5350$  A. with tolerable strength. The results are given in the subjoined Tables. In Table I under  $f$  cadmium and  $f$  lead are given the fractional parts of the order at the centre. They refer to the lines cadmium  $\lambda = 5986$  A. and lead  $\lambda = 4058$  A. The Table is divided into three sections comprising respectively the values obtained for cadmium and ordinary lead, cadmium and lead from pitchblende, and cadmium and lead from

Table I.

Plate.	Cadmium and ordinary lead		Cadmium and lead from pitchblende.		Cadmium and lead from thorite.	
	$f$ cadmium.	$f$ lead.	$f$ cadmium.	$f$ lead	$f$ cadmium.	$f$ lead.
1	0·954	1·130	0·945	1·005	0·644	0·518
2	0·939	1·136	0·938	1·064	0·640	0·516
3	0·944	1·139	0·938	1·063	0·629	0·516
4	0·940	1·120	0·937	1·068	0·628	0·510
5	0·933	1·134	0·938	1·058	0·618	0·498
6	0·956	1·127	0·928	1·054	0·626	0·505
Ordinary lead. $f$ reduced to $f$ Cd = 1·00.		Lead from pitchblende, $f$ reduced to $f$ Cd = 1·00.		Lead from Thorite. $f$ reduced to $f$ Cd = 2·00.		
1·188		1·134		1·218		
1·213		1·142		1·221		
1·209		1·141		1·235		
1·195		1·147		1·230		
1·218		1·136		1·231		
1·182		1·144		1·228		
Mean = 1·201 ± 0·006		1·141 ± 0·002		1·227 ± 0·0026		

Thickness of *étalon* = 9·80 mm. =  $d$ . Change in  $\lambda$  corresponding to a change in  $f$  of 1·00 =  $\lambda^2/2d = 0·084$  A.

$f$  (ordinary lead) —  $f$  (lead from pitchblende) =  $0·060 \pm 0·008$ .

$f$  (thorite lead) —  $f$  (ordinary lead) =  $0·026 \pm 0·009$ .

$\lambda$  (lead from pitchblende) —  $\lambda$  (ordinary lead) =  $0·0050$  A.  $\pm 0·0007$  A.

$\lambda$  (ordinary lead) —  $\lambda$  (thorite lead) =  $0·0022$  A.  $\pm 0·0008$  A.

thorite. In the lower part of the Table are given the respective values of  $f$ , reduced to the standard of the same cadmium fringe. In the case of cadmium and ordinary lead, and cadmium and lead from pitchblende the standard is the next order greater than the order of the innermost fringe, and in the case of cadmium and thorite lead the values are reduced to the second order greater than the innermost fringe, owing to a readjustment of the plates between the experiments.

It has already been pointed out that a comparison of two sets of cadmium fringes leaves no doubt as to the identification of the order adopted as the standard. In Table II are given the results obtained for ordinary thallium, and thallium from pitchblende; they refer to the thallium line  $\lambda = 5350$  Å.

Table II.

Plate.	Cadmium and ordinary thallium.		Cadmium and thallium from pitchblende.	
	$f$ cadmium.	$f$ thallium.	$f$ cadmium.	$f$ thallium.
1	0.964	0.383	0.962	0.406
2	0.946	0.369	0.972	0.418
3	0.962	0.382	0.962	0.426
4	0.988	0.361	0.962	0.408
5	0.951	0.357	0.959	0.419
6	0.947	0.360	0.963	0.422
<hr/>				
Ordinary thallium $f$ reduced to $f$ Cd = 1.00.			Thallium from pitchblende. $f$ reduced to $f$ Cd = 1.00	
0.417			0.442	
0.420			0.445	
0.418			0.472	
0.420			0.446	
0.404			0.458	
0.410			0.457	
<hr/>			<hr/>	
Mean = $0.415 \pm 0.0026$			$0.453 \pm 0.0046$	

Thickness of *étalon* = 9.80 mm. =  $d$ .

Change in  $\lambda$  corresponding to a change in  $f$  of 1.00 =  $\lambda^2/2d = 0.146$  Å.

$f$  (ordinary thallium) -  $f$  (thallium from pitchblende) =  $-0.038 \pm 0.007$ .

$\lambda$  (ordinary thallium) -  $\lambda$  (thallium from pitchblende) =  $+0.0055$  Å  $\pm 0.0010$  Å.

It will be observed that the numbers under columns 2 and 4 of Table I exceed unity. The reason of this is that there was a diffuse circle representing a fringe in the centre of the ring system; this diffuse ring was unsuitable for measurement, and the fringes actually measured were therefore the second and fifth, instead of the first and fourth. The differences found between

$\lambda$  (ordinary lead) and  $\lambda$  (lead from pitchblende) agree within the limits of experimental error with the value found by Aronberg, and this confirmation of his result would seem to establish the reality of the difference. The line in lead from pitchblende has a slightly longer wave-length than in ordinary lead, whilst the wave-length of the line in thorite lead is somewhat shorter. They are thus arranged in the order of their atomic weights, and in the direction which would be anticipated by the analogy of corresponding lines in the spectra of different metals belonging to the same group in the periodic system. The actual magnitudes of the differences are perhaps doubtful in view of some uncertainty as to the purity of the isotopes.

Some attempts have been made to detect a doubling of the lines in a mixture of two isotopes with a Fabry and Perot sliding interferometer, with the plates set at an appropriate distance apart, but the physical width of the lines renders the results inconclusive, and causes the fringes to disappear entirely at a difference of path at which the fringes of one isotope should lie midway between the fringes of the other; this occurs in the case of ordinary lead. Further experiments in this direction are contemplated, and it may be possible to show that the line in the mixture is a doublet by another method of experiment.

It has long been suspected that some of the metals which occur in pitchblende may be of radioactive origin, and the results obtained for thallium would seem to imply that the thallium in pitchblende is an isotope and probably of greater atomic weight than ordinary thallium. The results for thallium cannot, however, be given the same weight as those relating to lead. For a rigorous comparison it would be necessary to isolate the pure metal, for the plates show numerous lines due to other substances, and it is possible that the measurements may be affected by a neighbouring line due to some other element, or even that there may be a small change in the wave-length of the line due to the presence of the impurities.

Burns\* has found that certain manganese lines occurring as impurities in the iron arc differ in wave-length from the lines given by a manganese salt in the carbon arc, and that some barium lines are affected in a similar way. Displacements of this kind appear to be rare,† but the possibility that the thallium line may be so affected cannot be entirely dismissed.

There is one other peculiarity to which attention may be drawn. In the case of the thallium fringes, in which the satellite is well separated from the main line, I was at once struck by the fact that the fringes seemed sharper in the case of the thallium from pitchblende than in the case of ordinary

\* 'Comptes Rendus,' vol. 156, p. 1976 (1913).

† Cf. Bilham, 'Astrophys. Journ.,' vol. 42, p. 469 (1915).

thallium. Prof. Lindemann has been good enough to examine these plates, and he is able to confirm the reality of the difference in sharpness, but it may perhaps be due to slight variations in pressure or the admixture of other elements, and it would not be safe to draw any conclusions from it. The results in the case of lead seem so definite that the spectroscope may yet prove to be a most valuable weapon in attacking the problem of isotopic elements.

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*The Scattering of X- and  $\gamma$ -Rays by Rings of Electrons—A Crucial Test of the Electron Ring Theory of Atoms.*

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1. It is generally admitted that the Electron Ring Theory of Atoms, based on the classical electrodynamics and mechanics, does not explain certain results of recent investigations respecting thermal radiation, photoelectric emissions, transformations between corpuscular and X-ray energies and spectrum series. All these phenomena involve the interaction of radiation in one form or another, not merely with electrons, but also with matter, not so much with matter in bulk as with material atoms, and the failure of the Electron Ring Theory to account for them may after all be due rather to our ignorance of atomic structure than to defects in the fundamental principles of the theory itself. Moreover the hypotheses proposed for the explanation of the phenomena in question, such as the Quantum hypothesis, themselves fail to account for other phenomena, such as interference, diffraction and polarisation, which are so familiar to us that the necessity of explaining them afresh is apt to be overlooked when a new theory is introduced. In view of the present unsatisfactory state of our theories and the indecisive character of our experimental knowledge a crucial experimental test of the Electron Ring theory is very much to be desired, especially one involving as little knowledge of atomic structure as possible. The object of the present investigation is to show that the phenomenon of the scattering of X- and  $\gamma$ -rays by matter affords a test of this kind and, moreover, if the issue of the test be favourable, supplies a means of investigating experimentally the arrangement of the electrons in at any rate the lighter atoms. By scattering is meant the redistribution in space without change of frequency of a portion

of the radiation incident on matter. For our purpose any radiation of altered frequency, generated by processes akin to fluorescence or phosphorescence, must be carefully distinguished from scattered radiation.

2. Many years ago Sir J. J. Thomson propounded his well-known theory of the scattering of X- and  $\gamma$ -rays by matter, based mainly on three assumptions: (1) X- and  $\gamma$ -rays consist of extremely thin and intense electromagnetic pulses; (2) scattering is due entirely to the comparatively mobile electrons of the atom, that due to the relatively inert residue being neglected; and (3) the electromagnetic forces exerted by the pulses on the electrons are so intense that the forces due to other electrons and to the residue of the atom may be left out of account. Two of the results of this theory are important for the purpose of comparison with those of the present investigation: (1) The fraction of the incident energy scattered in a direction making an angle  $\theta$  with the direction of propagation of the incident beam is proportional to  $1 + \cos^2\theta$ ; and (2) the energy scattered every second in all directions together is  $8\pi e^4 n / 3c^4 m^2$  times the intensity of the incident radiation for  $n$  electrons all of which scatter effectively, and it is independent of their arrangement. With the usual values,  $e/c = 1.59 \cdot 10^{-20}$  and  $e/cm = 1.76 \cdot 10^7 e.m.u.$ , the coefficient is equal to  $0.656 \cdot 10^{-24}$  per electron. If we assume that the hydrogen atom has a mass  $1.64 \cdot 10^{-24}$  gm. and contains one mobile electron, we find that the mass scattering coefficient of hydrogen is 0.40. If further we assume that the number of electrons in atoms other than the hydrogen atom is one-half of the atomic weight, we find that the mass scattering coefficients of elements other than hydrogen are all equal to 0.20.

3. Recent experiments contradict this theory of scattering in three respects: (1) although the distribution of scattered radiation actually observed agrees with the  $1 + \cos^2\theta$  formula for directions nearly transverse to the beam, the amount of energy scattered in the forward direction exceeds, and in the backward direction falls short of that given by the formula, so that there is considerable asymmetry fore and aft, increasing with the hardness of the incident rays; (2) the atomic scattering coefficient is not equal to 0.20 for all elements other than hydrogen and for all rays, but diminishes to a very much smaller value for the most penetrating  $\gamma$ -rays for aluminium, iron and lead (Ishino); and (3) scattering always appears to be accompanied by a change of type corresponding to a softening of the radiation (Flourance), but whether this effect is due to an admixture of softer fluorescent radiation or not, does not appear to be determined.

4. In view of this contradiction between Sir J. J. Thomson's theory and experiment I have endeavoured to develop a more complete theory of the scattering of X- and  $\gamma$ -rays, replacing the simple pulse theory adopted in his

first assumption by the wave theory, which has superseded it, but retaining his last two assumptions. The third assumption requires us to assume that the frequency of the incident radiation is large compared with the frequencies of the free vibrations of the mobile electrons in the atom; the limits, within which this assumption is satisfied with a sufficient approximation, can only be determined exactly by experiment in our present state of ignorance as to the structure of the atom, but a rough estimate can be got for rotating rings of electrons by using the angular velocity in place of the frequencies, since it is of the right order of magnitude according to the various theories of atomic structure proposed hitherto.

In addition to these three assumptions, we shall assume, for the purpose of the present investigation, that (4) the mobile electrons of the atom are arranged in coaxial rings of equidistant electrons, which are rotating with uniform angular velocities, usually different for different rings, though, as a particular case, one or more of the rings may be at rest, and (5) the velocity of each electron is so small compared with that of light that the effect of the magnetic forces of the waves, as well as the reaction due to radiation from the electron and the variation of its mass with speed, may be neglected. The fourth assumption is needed to ensure the permanence of the rings in spite of radiation, and is justified by the experiments of O. W. Richardson and of Einstein and de Haas on the gyrostatic momentum of magnetised substances. The fifth is made for the sake of simplicity, to avoid confusing the main lines of the theory with unnecessary detail, but there is some justification for it in the fact that theories of atomic structure, such as that of Bohr, assign values to  $\beta$ , the ratio of the velocity of an electron to that of light, which are only of the order 0.01 for hydrogen and other light atoms; it may possibly cease to afford a sufficient approximation for heavy atoms in which the variation of mass with speed has to be taken into account in calculations respecting the determination of their constitution from their X-ray spectra (Vegard).

5. In accordance with our first assumption, we shall treat the incident X- or  $\gamma$ -radiation as consisting of undamped trains of plane unpolarised waves; it may be stated at once that the theory based on this and the remaining assumptions given above is one of diffraction by the electrons, coupled together kinematically in a ring, and constituting, as it were, an electronic grating. For hydrogen it leads to the same result as the simple pulse theory; for atoms containing rings of more than one electron it gives fore and aft asymmetry of scattered radiation and a scattering coefficient, which assumes the simple pulse theory's value for waves of infinitely high frequency, but increases, as the frequency diminishes, through a series of

more and more accentuated minima and maxima to a value not much less than  $n$  times the simple pulse theory's value, where  $n$  is the number of electrons in the ring. Thus the theory does not account for the exceptionally small scattering observed by Ishino, nor for the softening of the rays found by Florence; but there is reason to suppose that both of these effects may be explained on the assumption that X- and  $\gamma$ -rays consist of damped wavetrains. This modification of the theory is being investigated at present.

*Specification of the Incident Radiation.*

6. For the sake of generality, we shall assume that the incident radiation consists of a large number of independent simultaneous, or, alternatively, successive trains of undamped, elliptically polarised, parallel, plane waves, distributed in such a way in space, or in time, as the case may be, as to produce on the whole unpolarised radiation.

Each constituent wavetrain is characterised by five parameters: (1) The frequency,  $\nu$ , the same for all. (2) The epoch,  $\epsilon$ , chosen so that the phase is  $\nu t + \epsilon$  for the wave which at time  $t$  happens to pass through the centre of the electron ring. We shall assume that  $\epsilon$  is on the average distributed uniformly over the whole range from 0 to  $2\pi$ . (3) and (4) The semiaxes,  $a$  and  $b$ , of the vibration ellipse. (5) The polarisation azimuth,  $\alpha$ , measured in the wave front from some convenient initial line to the semiaxes  $a$ . We shall suppose that  $\alpha$  also is on the average distributed uniformly over the whole range from 0 to  $2\pi$ . The assumptions respecting the distribution of  $\epsilon$  and  $\alpha$  are obviously needed to ensure the average unpolarised character of the radiation as a whole.

The electric and magnetic forces at the centre of the electron ring at time  $t$  have components, in the directions of the semiaxes OA, OB of the vibration ellipse, which are given by the equations

$$d_A = h_n = \sum a \cos(\nu t + \epsilon), \quad d_B = -h_A = \sum b \sin(\nu t + \epsilon) \quad (1)$$

where the summation is to be taken for all possible sets of values of  $\epsilon$ ,  $a$ ,  $b$ , and  $\alpha$ .

The average energy flux,  $I$ , is the sum of the several component fluxes on account of the independence of the corresponding wavetrains and the average distribution of their epochs and polarisation azimuths. Hence we have by Poynting's theorem

$$I = c(\overline{d_A h_B} - \overline{d_B h_A})/4\pi = \sum c(a^2 + b^2)/8\pi \quad (2)$$

where the bar denotes time averaging, and  $c$  is the velocity of light.

*Specification of the Scattering Electron Ring.*

7. Let the radius of the ring be  $\rho$ , the number of equidistant electrons  $n$ , their charge  $e$  e.s.u., their mass  $m$  and their uniform angular velocity  $\omega$ . Also let  $\beta = \omega\rho/c$ ; then according to assumption (5)  $\beta$  is so small that  $m$  may be treated as constant and used to represent the transverse or the longitudinal mass at pleasure.

The relative positions of the incident and scattered wavetrains and the electron ring are shown in fig. 1, which represents the surface of the sphere whose centre is the centre O of the electron ring, and whose radius is unity.

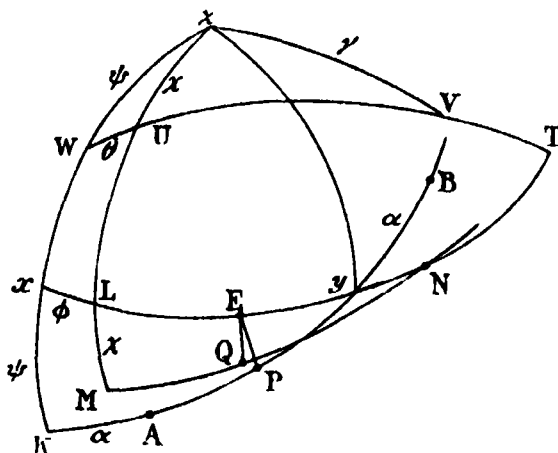


FIG. 1.

The great circle  $xy$  marks the plane of the ring, the direction of revolution being from  $x$  to  $y$ , and  $z$  marks its axis.  $E$  marks the radius vector to the  $i$ th electron at time  $t$ ; we take the arc  $xE$  to be equal to  $\omega t + \delta + 2\pi i/n$ , where  $i$  is any integer from 0 to  $n-1$ .

The great circle  $zx$  has been chosen to pass through  $W$ , which marks the direction of propagation of the wavetrains of the incident radiation;  $Ky$  marks that wave front of one of the trains, which happens to pass through the centre of the ring at time  $t$ , and  $A, B$  mark the semi-axes  $OA, OB$  of the vibration ellipse, so that  $KA = \alpha$ .

$U$  marks the direction in which the scattering takes place; the great circle  $MN$  marks that scattered wave front which passes through the centre of the electron ring at time  $t$ , and  $V$  marks the external bisector of the angle  $WOU$ —it is required for purposes of calculation later.

$EP$  is an arc of the great circle  $WEP$  drawn through  $E$  perpendicular to the incident wave front  $KY$ ; similarly  $EQ$  is an arc of the great circle  $UEQ$  drawn through  $E$  perpendicular to the scattered wave front  $MN$ .



8. We shall use the following notation :—

$$\begin{aligned} zW = xK = xyK = \psi, \quad zU = LM = LNM = \chi, \\ zV = \gamma, \quad WU = \theta, \quad \therefore zL = xzL = \phi. \end{aligned} \quad (3)$$

We shall require the perpendicular distances,  $p$  and  $q$ , of the electron  $E$  from the incident and scattered wave fronts  $K\gamma$  and  $MN$  respectively; these will be reckoned positive when the electron is in front of the respective wave front. Thus we obtain by means of fig. 1 and (3)

$$\left. \begin{aligned} p &= \rho \sin PE = \rho \sin E\gamma \sin xyK = \rho \sin \psi \cos(\omega t + \delta + 2\pi i/n) \\ q &= \rho \sin QE = \rho \sin EN \sin LNM = \rho \sin \chi \cos(\omega t + \delta + 2\pi i/n - \phi) \end{aligned} \right\}. \quad (4)$$

We shall require the value of  $p - q$  below; we find from (4)

$$\begin{aligned} p - q &= \rho \{ \sin \psi - \sin \chi \cos \phi \} \cos(\omega t + \delta + 2\pi i/n) \\ &\quad - \sin \chi \sin \phi \sin(\omega t + \delta + 2\pi i/n) \}. \end{aligned} \quad (5)$$

From (3) and fig. 1 we obtain

$$\begin{aligned} (\sin \psi - \sin \chi \cos \phi)^2 + \sin^2 \chi \sin^2 \phi &= \sin^2 \psi + \sin^2 \chi - 2 \sin \psi \sin \chi \cos \phi \\ &= 2(1 - \cos \theta) - (\cos \chi - \cos \psi)^2 \\ &= 4 \sin^2 \gamma \sin^2 \frac{1}{2} \theta, \end{aligned}$$

since we have

$$\cos \chi - \cos \psi = \cos \gamma (\cos UV - \cos WV) = 2 \cos \gamma \sin \frac{1}{2} \theta.$$

Hence we find from (5)

$$\begin{aligned} p - q &= 2\rho \sin \gamma \sin \frac{1}{2} \theta \cos(\omega t + \delta + \nu + 2\pi i/n), \\ \nu &= \tan^{-1} \frac{\sin \chi \sin \phi}{\sin \psi - \sin \chi \cos \phi}. \end{aligned} \quad (6)$$

This result will be required presently.

### *The Electric Forces of the Incident and Scattered Waves.*

9. In order to find the scattered radiation we must determine the electromagnetic field at a distant point due to the disturbance of the electron generated by the incident waves.

Let the field point be in the direction of the unit vector  $\mathbf{U}$  at a great distance  $R$  from the centre of the electron ring; its distance from the electron  $E$  is equal to  $R - q$  very approximately.

Also let  $\mathbf{f}$  denote the acceleration of the electron; then we know that to the same approximation the electric and magnetic forces at the field point at time  $t$  are given by

$$\mathbf{d} = -\frac{e}{c^2 R} \{ \mathbf{f} - (\mathbf{U} \mathbf{f}) \mathbf{U} \}_{t - (R - q)/c}, \quad \mathbf{h} = [\mathbf{U} \mathbf{d}]. \quad (7)$$

Terms of the relative order  $q/R$  have been neglected in calculating *intensities*, but they must be retained in estimating *phases*, so that the function inside the bracket in the expression for  $\mathbf{d}$  must be taken for the time  $t - (R - q)/c$ , not for the time  $t - R/c$ , in order to calculate the diffraction effect.

10. In order to calculate the acceleration  $\mathbf{f}$  of the electron due to the incident waves we must bear in mind our assumptions (3), § 2, and (5), § 4. In virtue of (3) we need only retain the effective force due to the incident waves on the left of the vector equation of motion, neglecting the effective force due to steady revolution as well as the controlling forces due to the remaining electrons of the ring and the residue of the atom. In virtue of (5) we may on the left take the mass of the electron to be the constant  $m$ , and on the right neglect the effect of the magnetic forces of the incident waves. Denoting the electric force of the incident wave at the *undisturbed* position of the electron at the time of emission by  $\mathbf{d}'$  for the moment, we may write

$$m\mathbf{f} = c\mathbf{d}'. \quad (8)$$

In writing down this equation we have neglected the effect of the disturbance on the mass of the disturbed electron and have used the *undisturbed* instead of the *disturbed* position of the electron at the time of emission in calculating the electric force which generates the disturbance. The error is of the order of the square of the disturbing force in each case; we shall neglect errors of this order throughout for the sake of simplicity.

11. We must now find the value of the disturbing electric force  $\mathbf{d}'$  at the undisturbed position of the electron at the time of emission. We commence by finding its components at the centre of the electron ring at the time  $t$  by means of (1), § 6, and fig. 1, § 7. Resolving the electric force in the directions OK, O*x*, O*y*, and O*z* we obtain

$$\left. \begin{aligned} d_x' &= \Sigma \{a \cos \alpha \cos (\nu t + \epsilon) - b \sin \alpha \sin (\nu t + \epsilon)\} \\ &= \frac{1}{2} \Sigma (a \cos \alpha + ib \sin \alpha) \exp i(\nu t + \epsilon) \\ d_y' &= \Sigma \{a \sin \alpha \cos (\nu t + \epsilon) + b \cos \alpha \sin (\nu t + \epsilon)\} \\ &= \frac{1}{2} \Sigma (a \sin \alpha - ib \cos \alpha) \exp i(\nu t + \epsilon) \\ d_z' &= d_\kappa \cos \psi, d_z' = -d_\kappa \sin \psi \end{aligned} \right\}, \quad (9)$$

where the conjugate terms have been omitted for the sake of brevity.

Clearly (9) give the components of the electric force  $\mathbf{d}'$  at the undisturbed position of the electron E at the time  $t$ , provided that we replace  $t$  in (9) by  $t - p/c$ , because every incident wave front reaches E at a time later by the amount  $p/c$ , where  $p$  is given by (4), § 8, for the time  $t$ .

Also (8), § 10, gives the corresponding acceleration at time  $t$ . Hence we

find that the acceleration due to the disturbance of the  $i$ th electron  $\mathbf{E}$  at time  $t$  is given by

$$\left. \begin{aligned} f_x &= \frac{e \cos \psi}{2m} \sum (a \cos \alpha + ib \sin \alpha) \exp i \{ \nu(t-p/c) + \epsilon \} \\ f_y &= \frac{e}{2m} \sum (a \sin \alpha - ib \cos \alpha) \exp i \{ \nu(t-p/c) + \epsilon \} \\ f_z &= -\frac{e \sin \psi}{2m} \sum (a \cos \alpha + ib \sin \alpha) \exp i \{ \nu(t-p/c) + \epsilon \} \end{aligned} \right\} \quad (10)$$

with  $p = \rho \sin \psi \cos (\omega t + \delta + 2\pi i/n)$

12. In calculating the electric and magnetic forces of the scattered wave by means of (7), § 9, we must not take the components of  $\mathbf{f}$  for the time  $t$  when the wave arrives at the field point, but for the time  $t - (R-q)/c$  when it is emitted by the scattering electron, so that we must replace  $t$  in (10), § 11, by  $t - (R-q)/c$ , and calculate  $q$  by (4), § 8, with  $t - R/c$  in place of  $t$ . Thus in place of (10) we must use the following equations:—

$$\left. \begin{aligned} f_x &= \frac{e \cos \psi}{2m} \sum (a \cos \alpha + ib \sin \alpha) \exp i \{ \nu(t-R/c) + \epsilon - \nu(p-q)/c \} \\ f_y &= \frac{e}{2m} \sum (a \sin \alpha - ib \cos \alpha) \exp i \{ \nu(t-R/c) + \epsilon - \nu(p-q)/c \} \\ f_z &= -\frac{e \sin \psi}{2m} \sum (a \cos \alpha + ib \sin \alpha) \exp i \{ \nu(t-R/c) + \epsilon - \nu(p-q)/c \} \\ p &= \rho \sin \psi \cos \{ \omega(t-R/c) + \delta + 2\pi i/n + \omega q/c \} \\ q &= \rho \sin \chi \cos \{ \omega(t-R/c) + \delta + 2\pi i/n - \phi \} \end{aligned} \right\} \quad (11)$$

13. At this stage a difficulty requires notice, which arises from the occurrence of the term  $\omega q/c$  in the argument of the cosine in  $p$ . With the usual notation of Bessel Functions, bearing in mind that  $\omega \rho/c$  is equal to  $\beta$ , we may write

$$\begin{aligned} p &= \text{Real part of } \rho \sin \psi \exp i \{ \omega(t-R/c) + \delta + 2\pi i/n + \omega q/c \} \\ &= \text{Real part of } \rho \sin \psi \exp i \{ \omega(t-R/c) + \delta + 2\pi i/n \} \\ &\quad \sum_{-\infty}^{\infty} J_j(\beta \sin \chi) \exp i \{ \omega(t-R/c) + \delta + \frac{1}{2}\pi + 2\pi i/n - \phi \}. \end{aligned}$$

Owing to the smallness of  $\beta$  we may neglect all the Bessel Functions except  $J_0(\beta \sin \chi)$  and replace this by unity; this amounts to neglecting the term  $\omega q/c$  in the argument of  $p$  because it is of the order  $\beta$ .

Obviously we cannot do this with the term  $\nu(p-q)/c$  in the argument of  $(f_x, f_y, f_z)$  of (11), because  $\nu$  is assumed to be large in comparison with  $\omega$ , but

we may use (6), § 8, in place of (4), with  $t-R/c$  in place of  $t$ , so that we may write

$$\nu(p-q)/c = 2\tau \sin \gamma \sin \frac{1}{2} \theta \cos \{ \omega(t-R/c) + \delta + \nu + 2\pi i/n \} \quad (12)$$

where  $\tau = \nu\rho/c = 2\pi\rho/\lambda$

This equation, together with the first three equations (11), § 8, determines the values of the components of  $\mathbf{f}$  to be substituted in (7), § 9.

14. By means of the well-known Bessel Function expansion we obtain from (12), § 13,

$$\begin{aligned} \exp \{ -i\nu(p-q)/c \} &= \exp 2i\tau \sin \gamma \sin \frac{1}{2} \theta \\ &\quad \sin \{ \omega(t-R/c) + \delta + \nu - \frac{1}{2} \pi + 2\pi i/n \} \\ &= \sum_{-\infty}^{\infty} J_j(2\tau \sin \gamma \sin \frac{1}{2} \theta) \\ &\quad \exp i j \{ \omega(t-R/c) + \delta + \nu - \frac{1}{2} \pi + 2\pi i/n \}. \end{aligned} \quad (13)$$

Substituting from (13) in (11), § 12, we find

$$\begin{aligned} \mathbf{f} &= \frac{e}{2m} \sum_{-\infty}^{\infty} \{ \cos \psi(a \cos \alpha + ib \sin \alpha), a \sin \alpha - ib \cos \alpha, \\ &\quad -\sin \psi(a \cos \alpha + ib \sin \alpha) \} J_j(2\tau \sin \gamma \sin \frac{1}{2} \theta) \\ &\quad \exp i \{ (\nu + j\omega)(t-R/c) + \epsilon + j(\delta + \nu - \frac{1}{2} \pi + 2\pi i/n) \}. \end{aligned} \quad (14)$$

Since the components of the unit vector  $\mathbf{U}$  are  $\sin \chi \cos \phi$ ,  $\sin \chi \sin \phi$ , and  $\cos \chi$  respectively, whilst in fig. 1, § 7,  $\cos KU = \cos \psi \sin \chi \cos \phi - \sin \psi \cos \chi$ , and  $\cos yU = \sin \chi \sin \phi$ , we obtain from (14)

$$\begin{aligned} (\mathbf{U}\mathbf{f}) &= \frac{e}{2m} \sum_{-\infty}^{\infty} \{ \cos KU(a \cos \alpha + ib \sin \alpha) + \cos yU(a \sin \alpha - ib \cos \alpha) \} \\ &\quad J_j(2\tau \sin \gamma \sin \frac{1}{2} \theta) \exp i \{ (\nu + j\omega)(t-R/c) + \epsilon + j(\delta + \nu - \frac{1}{2} \pi + 2\pi i/n) \}. \end{aligned} \quad (15)$$

These expressions, (14) and (15), when they are substituted in (7), § 9, give the electric and magnetic forces at the distant point due to the waves scattered by the  $i$ th electron. To obtain those due to the whole ring we must sum the resulting expressions for all values of  $i$  from 0 to  $n-1$ , but since the forces are linear functions of the quantities  $\mathbf{f}$  and  $(\mathbf{U}\mathbf{f})$ , we obtain the same result by first performing the summation on the expressions (14) and (15), and then substituting the sums in (7). We notice that the specimen terms given in (14) and (15) involve the factor  $\exp i 2\pi i j/n$ , the sum with respect to  $i$  from 0 to  $n-1$  of each such factor vanishes identically for all values of  $j$ , with the exception of those of the form  $kn$ , where  $k$  is an integer, and in these cases the exponential reduces to unity for every value of  $i$ , and the sum to  $n$ . Thus the required sums are obtained from (14) and (15) by

changing  $j$  into  $kn$  and multiplying each expression by  $n$ . It is hardly worth while to write down their actual expressions, as the indications just given suffice for our purpose.

*The Scattered Radiation.*

15. To find the amount of the radiation scattered by the ring in the direction of the unit vector  $\mathbf{U}$ , we apply Poynting's theorem. From (7), § 9, we obtain for the Poynting flux due to the whole ring

$$\mathbf{P} = \frac{c}{4\pi} [\mathbf{d}\mathbf{h}] = \frac{c}{4\pi} d^2 \mathbf{U} = \frac{e^2}{4\pi c^3 R^2} [\{\Sigma \mathbf{f}\}^2 - \{\Sigma (\mathbf{U}\mathbf{f})\}^2] \mathbf{U}, \quad (16)$$

where the summation indicated by the symbol  $\Sigma$  is with respect to  $i$  and is performed in the manner indicated at the end of § 14.

The radiation scattered per unit solid angle in the direction  $\mathbf{U}$ , to be denoted by the symbol  $P$  in future, is obtained by multiplying the coefficient of  $\mathbf{U}$  in the expression (16) for  $\mathbf{P}$  by  $R^2$  and averaging the result with respect to the time  $t$  and the polarisation azimuth  $\alpha$ . In the time averaging all squares and products of exponentials vanish identically with the sole exception of products of conjugate exponentials, so that the epochs  $\epsilon$  and  $\delta$ , as well as the angle  $\nu$  disappear in the process. In averaging with respect to  $\alpha$  the product  $\sin \alpha \cos \alpha$  vanishes, and the squares  $\cos^2 \alpha$  and  $\sin^2 \alpha$  reduce each to one-half on account of the unpolarised character of the incident radiation as a whole. Bearing in mind what was said at the end of § 14 as to the sums with respect to  $i$  of  $\mathbf{f}$  and  $(\mathbf{U}\mathbf{f})$ , we obtain by means of (14), (15), and (16), in the first instance,

$$P = \frac{e^4 n^2}{8\pi c^3 m^2} \Sigma \Sigma_{-\infty}^{\infty} (a^2 + b^2) \{1 - \frac{1}{2}(\cos^2 KU + \cos^2 yU)\} J_{kn}^2 (2\tau \sin \gamma \sin \frac{1}{2} \theta). \quad (17)$$

The first summation is for all values of  $a$  and  $b$ , since the remaining parameters of the incident radiation,  $\nu$ ,  $\epsilon$ , and  $\alpha$ , have all disappeared; thus  $\Sigma(a^2 + b^2)$  enters into (17) as a factor, and by (2), § 6, its value is  $8\pi I/c$ . Moreover, we see from fig. 1, § 7, that

$$\cos^2 KU + \cos^2 yU = \sin^2 WU = \sin^2 \theta.$$

Hence (17) gives

$$P = I \frac{e^4 n^2}{2c^4 m^2} (1 + \cos^2 \theta) \Sigma_{-\infty}^{\infty} J_{kn}^2 (2\tau \sin \gamma \sin \frac{1}{2} \theta). \quad (18)$$

16. The infinite summation with respect to  $k$  can be replaced by a finite one with respect to  $i$ , for we have the well-known equation

$$J_{kn}^2 (2\tau \sin \gamma \sin \frac{1}{2} \theta) = \frac{1}{\pi} \int_0^\pi J_0 (4\tau \sin \gamma \sin \frac{1}{2} \theta \sin \phi) \cos 2kn\phi d\phi.$$

Hence we obtain in succession by means of Dirichlet's discontinuous integral

$$\begin{aligned}\sum_{n=1}^{\infty} J_n^2(2\tau \sin \gamma \sin \frac{1}{2} \theta) &= \frac{1}{\pi} \int_0^\pi J_0(4\tau \sin \gamma \sin \frac{1}{2} \theta \sin \phi) \sum_{n=-\infty}^{\infty} \cos 2kn \phi d\phi \\ &= \frac{1}{\pi} \lim_{k \rightarrow \infty} \int_0^\pi J_0(4\tau \sin \gamma \sin \frac{1}{2} \theta \sin \phi) \frac{\sin(2k+1)n\phi}{\sin n\phi} d\phi \\ &= \frac{1}{n} \sum_{i=0}^{n-1} J_0\left(4\tau \sin \frac{\pi i}{n} \sin \gamma \sin \frac{1}{2} \theta\right)\end{aligned}$$

Substituting this result in (18), separating the term  $i = 0$  from the rest and replacing the ratio  $P/I$  by  $s$ , we obtain for the scattering coefficient in the direction  $\mathbf{U}$  the expression

$$s = \frac{e^4 n}{2c^4 m^2} (1 + \cos^2 \theta) \left\{ 1 + \sum_{i=1}^{n-1} J_0\left(4\tau \sin \frac{\pi i}{n} \sin \gamma \sin \frac{1}{2} \theta\right) \right\}. \quad (19)$$

Thus  $s$ , the scattering coefficient per unit solid angle is determined by (19) as a function of two variables only, viz.,  $\theta$ , the angle between the incident and scattered beams, and  $\gamma$ , the angle between the axis of the scattering electron ring and the external bisector  $OV$  of the angle  $\theta$ , which is shown in fig. 1, § 7. The radius  $\rho$  of the ring and the wave-length  $\lambda$  of the incident vibration only enter into the expression for  $s$  implicitly through the parameter  $\tau$ , which is equal to  $2\pi\rho/\lambda$  by (12), § 13. The form of the result depends essentially on  $n$ , the number of electrons in the ring. When there is but one electron,  $n = 1$ , the sum disappears, and (19) gives

$$s = \frac{e^4}{2c^4 m^2} (1 + \cos^2 \theta). \quad (20)$$

In this case, and this case alone, the scattering coefficient is independent of  $\gamma$ , which determines the position of the ring relative to the incident beam, and is simply proportional to  $1 + \cos^2 \theta$ , in agreement with the simple pulse theory. We have every reason for assuming that this is the case of the hydrogen atom.

Thus scattering experiments on hydrogen, either gas under pressure or liquid, with a sufficiently extended range of wave-lengths would enable us to test (20), but such experiments alone could not decide between the simple pulse theory and the present one.

17. When the argument of the Bessel Function in (19), § 16, is zero, that function reduces to unity and we obtain

$$s = \frac{e^4 n^2}{2c^4 m^2} (1 + \cos^2 \theta). \quad (21)$$

This occurs in three cases:—

(i) When  $\tau$  vanishes, *i.e.*, when the wave-length,  $\lambda$ , of the incident radiation is infinitely great in comparison with  $\rho$ , the radius of the electron ring. This case is never actually realised, because resonance sets in when  $\lambda$  becomes large enough, and assumption (3) is violated; but, owing to the flatness of the first maximum of the Bessel Function  $J_0$ , it can be approached very nearly, and we may therefore expect an increase of the scattering coefficient as the wave-length increases to values considerably greater than the value given by the simple pulse theory, and in fact not much less than  $n$  times that value.

(ii) When  $\gamma$  is 0 or  $\pi$ , *i.e.*, when the plane of the electron ring bisects the angle between the incident and scattered beams. This case might conceivably be realised with an assemblage of magnetic atoms by applying a strong magnetic field in the direction of the external bisector of the incident and scattered beams; at any rate, an increased scattering might be obtained, if not the full amount of  $n$  times the simple pulse theory's value.

(iii) When  $\theta$  is 0, *i.e.*, in the forward direction of the incident beam, a case which merits special consideration.

#### *Forward and Backward Scattering.*

18. Putting  $\theta = 0$  in (21), § 17, we obtain for the forward scattering

$$s_f = \frac{e^4 n^2}{c^4 m^2}, \quad (22)$$

which is exactly  $n$  times the simple pulse theory's value for every wave-length and all orientations of the electron ring.

Again, putting  $\theta = \pi$  in (19), § 16, we obtain for the backward scattering

$$s_f = \frac{e^4 n}{c^4 m^2} \left\{ 1 + \sum_1^{n-1} J_0 \left( 4\tau \sin \frac{\pi i}{n} \sin \gamma \right) \right\}. \quad (23)$$

The effect of the sum in (23) is most pronounced when  $\gamma = \pi/2$ . This case might be realised approximately by using a magnetic substance in a strong magnetic field perpendicular to the incident beam, and observing the scattering in a direction as nearly as possible opposite to the direction of propagation of the incident beam.

The simplest example is given by the value  $n = 2$ , which probably corresponds to the helium atom; we obtain from (22) and (23)

$$s_f = \frac{4e^4}{c^4 m^2}, \quad s_f = \frac{2e^4}{c^4 m^2} \{ 1 + J_0(4\tau \sin \gamma) \}. \quad (24)$$

The first and lowest minimum of  $J_0(4\tau \sin \gamma)$  is equal to  $-0.403$  and is given by  $4\tau \sin \gamma = 3.83$ , or  $\lambda = 6.56 \rho \sin \gamma$ . For this value of  $\lambda$ ,  $s_f$  is less

than 30 per cent. of  $s_f$ , so that the asymmetry fore and aft is considerable. For greater values of  $n$  it may become still more marked.

Qualitative experiments with magnetic substances in strong magnetic fields of the kind indicated in this and the preceding section would enable us to decide between the simple pulse theory and the present one, but not between the latter and a theory based on the Parson ring electron, because the Parson ring electron gives rise to analogous magnetic effects.

#### *Scattering due to an Assemblage of similar Electron Rings.*

19. In order to calculate the average scattering of an assemblage of electron rings, we must make a further assumption (6): each electron ring scatters the incident radiation independently of all the other rings. Actually the radiation scattered by any one ring falls on others and is scattered by them; our assumption amounts to neglecting the proportion of radiation which undergoes double, triple, and in general multiple scattering. It is obvious that the effect of multiple scattering will be to diffuse the radiation and partially destroy the asymmetry produced by a single scattering, and will be greater the denser and thicker the assemblage is. Its existence might be detected experimentally by working with gases at different pressures; its effect might be made comparatively harmless by working with thin layers of material, or by using layers of varying thickness and extrapolating for infinitesimal thickness in the usual manner.

We shall only consider the simplest case, where the axes of the electron rings are on the average distributed equally in all directions. To find the average scattering  $\bar{s}$  in the direction  $\mathbf{U}$ , we multiply (19), § 16, by the chance that the angle  $\gamma$  should lie between the limits  $\gamma$  and  $\gamma + d\gamma$ , viz.  $\frac{1}{2} \sin \gamma d\gamma$ , and integrate with respect to  $\gamma$  from 0 to  $\pi$ . Thus we obtain, most simply by expanding the Bessel Function and integrating term by term,

$$\bar{s} = \frac{e^4 n}{2c^2 m^2} (1 + \cos^2 \theta) \left\{ 1 + \sum_1^{n-1} \sin \left( 4\tau \sin \frac{\pi i}{n} \sin \frac{1}{2} \theta \right) / 4\tau \sin \frac{\pi i}{n} \sin \frac{1}{2} \theta \right\}. \quad (25)$$

This expression leads to similar results as regards asymmetry as (19), § 16, though, as is to be expected, they are not quite so marked. In the forward direction,  $\theta = 0$ , the scattering is  $n$  times the simple pulse theory's value as before, but in the backward direction,  $\theta = \pi$ , the Bessel Function term in (23), § 18, is replaced by  $\sin \left( 4\tau \sin \frac{\pi i}{n} \right) / 4\tau \sin \frac{\pi i}{n}$ . This term, too, is oscillatory; its first and lowest minimum is equal to  $-0.217$  and corresponds to  $4\tau \sin \frac{\pi i}{n} = 4.49$ . For the two-electron ring of helium the backward scattering,  $\bar{s}_b$ , is 39 per cent. of the forward scattering,  $\bar{s}_f$ , and occurs for  $\lambda = 5.60\rho$ .



*Scattering of an Irregular Assemblage of Rings through a Finite Solid Angle.*

20. We shall calculate the total scattering through the front half of a cone of semivertical angle  $\theta$ , with its axis parallel to the direction of the incident beam, and for this purpose multiply (25), § 19, by  $2\pi \sin \theta d\theta$  and integrate from 0 to  $\theta$ . The integration is best performed by changing the variable from  $\theta$  to  $u \equiv \sin \frac{1}{2}\theta$ . Denoting the total scattering through the cone by  $S(\theta)$ , we obtain

$$S(\theta) = \frac{8\pi e^4 n}{3c^4 m^2} \left\{ u^6 + \frac{3}{2} u^2 (1-u^2) + \sum_1^{n-1} \frac{3}{4r^2} \left[ 1 + \frac{1}{r^2} + \frac{3}{r^4} - \left( 1 - 2u^2 + 2u^4 + \frac{1-6u^2}{r^2} + \frac{3}{r^4} \right) \cos 2ru - \frac{2u}{r} \left( 1 - 2u^2 + \frac{3}{r^2} \right) \sin 2ru \right] \right\} \quad (26)$$

where  $u = \sin \frac{1}{2}\theta$ ,  $r = 2\tau \sin \frac{\pi i}{n} = \frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n}$

Adopting the notation of 'R. A. Report,' 1914, p. 87, we write

$$S_0(x) = \sin x, \quad S_1(x) = \frac{\sin x}{x} - \cos x, \quad S_2(x) = \left( \frac{3}{x^2} - 1 \right) \sin x - \frac{3}{x} \cos x. \quad (27)$$

Then we may write (26) in the form

$$S(\theta) = \frac{8\pi e^4 n}{3c^4 m^2} u^2 \left\{ u^4 \left[ 1 + \sum_1^{n-1} \{ S_0^2(ru) + \frac{1}{2} S_2^2(ru) \} r^{-2} u^{-2} \right] + \frac{3}{2} (1-u^2) \left[ 1 + \sum_1^{n-1} \{ S_0^2(ru) + u^2 S_1^2(ru) \} r^{-2} u^{-2} \right] \right\}. \quad (28)$$

We shall consider two important particular cases of this formula.

*Total Scattering.*

21. The total scattering from the ring is obtained by putting  $\theta = \pi$ , or  $u = 1$ , in (28), § 20. In this case we shall omit the argument  $\pi$  of  $S(\pi)$  as unnecessary and obtain

$$S = \frac{8\pi e^4 n}{3c^4 m^2} \left\{ 1 + \sum_1^{n-1} f\left(\frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n}\right) \right\} \quad (29)$$

where  $f(x) = \{ S_0^2(x) + \frac{1}{2} S_2^2(x) \} x^{-2}$

For hydrogen we assume that  $n = 1$ , so that the sum disappears. Denoting the corresponding value by  $S_u$ , we find

$$S_u = \frac{8\pi e^4}{3c^4 m^2} = 0.656 \cdot 10^{-24}, \quad (30)$$

where the numerical values are the same as those used in § 2. The result is precisely that of the simple pulse theory, so that on both theories the

scattering of hydrogen is independent of the wave-length, and its distribution is symmetrical fore and aft.

It is convenient to take hydrogen as the standard to which all other substances are referred.

*Atomic and Mass Scattering Coefficients.*

22. An atom is assumed to contain coaxial rings of equidistant mobile electrons (§ 3, assumption (3)). We shall neglect the possibility that two rings may have a constant phase relation between them, and so interfere with each other; this occurs when they have the same angular velocity, a contingency which is extremely unlikely on any of the current theories of atomic structure. Then the scattering of an atom is the sum of the scatterings of its several electron rings.

Let the atomic number be  $N$  so that

$$N = \sum n, \quad (31)$$

where the summation is for all the rings. We obtain from (29) and (30), § 21,

$$S = S_H \left\{ N + \sum n \sum_1^{n-1} f \left( \frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n} \right) \right\} \quad (32)$$

Experimenters often use the mass scattering coefficient, *i.e.*, the scattering per unit mass, in place of  $S$ , which denotes the scattering per atom, or atomic scattering coefficient. We shall denote the mass scattering coefficient by  $\sigma$ , and that of hydrogen by  $\sigma_H$ ; to obtain them we must divide by the mass of the atom. Taking the mass of the hydrogen atom to be  $1.64 \cdot 10^{-24}$  grm., we find from (30), § 21,

$$\sigma_H = 0.40. \quad (33)$$

Since the mass of an atom of atomic weight  $A$  is  $A$  times the mass of the hydrogen atom, we obtain from (32) and (33)

$$\sigma = \frac{0.40}{A} \left\{ N + \sum n \sum_1^{n-1} f \left( \frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n} \right) \right\}. \quad (34)$$

For molecules of compound substances we must add together the atomic scattering coefficients  $S$  of its constituents, and divide  $\sum S$  by  $\sum A$ , in order to obtain the mass scattering coefficient.

One important result of (34) should be noticed; when the wave-length  $\lambda$  of the incident radiation becomes very great, the argument of the function  $f$  becomes very small, and the function itself becomes very nearly equal to unity, as we shall see below.

Hence we find

$$\lim_{n \rightarrow \infty} \sigma = \frac{0.40}{A} \Sigma n^2. \quad (35)$$

The simple pulse theory gives  $\sigma = 0.40NA^{-1}$  for all wave-lengths, so that the present theory gives a very much larger value for long waves, although it gives the same value for very short waves.

The long wave limit cannot be reached owing to the intervention of resonance, but it can be approached pretty closely, say within 10 or 20 per cent., long before resonance becomes appreciable, so that measurements of scattering for long waves should enable us to decide between the two theories.

Before considering particular examples of the theory, we shall first consider the second particular case of formula (28), § 20.

#### *Emergent and Returned Scattered Radiation.*

23. Florence defines emergent scattered radiation as that which is scattered forwards on the whole, i.e., between the limits  $\theta = 0$  and  $\theta = \frac{1}{2}\pi$ , and returned scattered radiation as that which is scattered backwards on the whole, i.e., between the limits  $\theta = \frac{1}{2}\pi$  and  $\theta = \pi$ . We shall denote the corresponding atomic and mass scattering coefficients by  $S_e$ ,  $S_r$ , and  $\sigma_e$ ,  $\sigma_r$ , respectively.

Putting  $\theta = \frac{1}{2}\pi$ ,  $u = \frac{1}{\sqrt{2}}$  in (28), § 20, and using (30), § 21, we obtain for a single ring

$$\left. \begin{aligned} S_e &= \frac{1}{2} S_n n \left\{ 1 + \sum_1^{n-1} \left[ f\left(\frac{r}{\sqrt{2}}\right) + g\left(\frac{r}{\sqrt{2}}\right) \right] \right\} \\ \text{where} \quad g(x) &= \frac{1}{2} \{ S_1^2(x) - S_2^2(x) \} x^{-2} \\ \text{while} \quad r &= \frac{4\pi\sigma}{\lambda} \sin \frac{\pi i}{n} \end{aligned} \right\} \quad (36)$$

and  $f(x)$  is given by (29), § 21, as before.

The value of  $S_r$  is clearly  $S - S_e$ , but for our purpose it is more convenient to use the difference  $S_e - S_r$ , which we shall denote by  $E$ . From (36) together with (29) and (30), § 21, we obtain

$$\left. \begin{aligned} E &= S_n n \sum_1^{n-1} h(r) \\ \text{where} \quad h(r) &= f\left(\frac{r}{\sqrt{2}}\right) + g\left(\frac{r}{\sqrt{2}}\right) - f(r), \quad r = \frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n} \end{aligned} \right\} \quad (37)$$

Proceeding just as before in § 22 we obtain for the mass coefficients of an atom of atomic number  $N$  and atomic weight  $A$

$$\eta = \frac{0.40}{A} \sum n \sum_1^{n-1} h(r), \quad \sigma_e = \frac{1}{2}(\sigma + \eta), \quad \sigma_r = \frac{1}{2}(\sigma - \eta), \quad (38)$$

where  $\sigma$  is given by (34), § 22.

The coefficient  $\eta$  may be taken as an absolute measure of the fore and aft asymmetry of the atom on the same scale on which  $\sigma$  measures the total scattering; a relative measure would be afforded by the ratio  $\eta : \sigma$ , but the variation of this ratio with the wave-length differs so little from that of  $\eta$  itself that it is hardly worth while to introduce it in addition. The asymmetry is reckoned positive when  $\eta$  is positive, *i.e.*, when the emergent exceeds the returned scattered radiation, which is usually the case.

#### Numerical Values of the Coefficients.

24. For convenience sake, we collect the principal expressions which are of use for the purpose of comparison with experimental results, *viz.*, (34), § 22, for the mass scattering coefficient  $\sigma$ , and (37) and (38), § 23, for the asymmetry coefficient  $\eta$ . They are

$$\left. \begin{aligned} \sigma &= \frac{0.40}{A} \left\{ N + \sum n \sum_1^{n-1} f(r) \right\}, & f(r) &= \{S_0^2(r) + \frac{1}{2} S_2^2(r)\} r^{-2} \\ \eta &= \frac{0.40}{A} \sum n \sum_1^{n-1} h(r), & h(r) &= f\left(\frac{r}{\sqrt{2}}\right) + g\left(\frac{r}{\sqrt{2}}\right) - f r, \\ & & g(r) &= \frac{2}{3} \{S_1^2(r) - S_2^2(r)\} r^{-2} \end{aligned} \right\}. \quad (39)$$

where  $r = \frac{4\pi\rho}{\lambda} \sin \frac{\pi i}{n}$

The functions  $f(r)$  and  $h(r)$  are fundamental for the theory, whilst the function  $g(r)$  is useful as an intermediary for purposes of calculation. Tables of these functions are given at the end of this paper for values of  $r$  from 0 to 10, and graphs of  $f(r)$  and  $h(r)$  are given in fig. 2 between the same limits.

We see that  $f(r)$  has a sharp maximum equal to unity when  $r = 0$ , a low minimum equal to 0.046 when  $r = 3.1$ , a comparatively low maximum equal to 0.076 nearly when  $r = 4.02$ , a very low minimum equal to 0.002 when  $r = 6.1$ , and so on, fluctuating between diminishing positive limits, and ultimately vanishing when  $r$  becomes infinitely great.

On the other hand,  $h(r)$  vanishes when  $r = 0$ , has a fairly sharp maximum equal to 0.320 nearly when  $r = 2.1$ , a small negative minimum equal to -0.022 when  $r = 4.5$ , a small maximum equal to 0.051 when  $r = 6.2$ , and so

on, fluctuating between diminishing alternately positive and negative limits and ultimately vanishing when  $r$  becomes infinitely great. We notice that negative asymmetry occurs for certain ranges of wave-length.

*Comparison with Experiment.*

25. In order to test the correctness of the theory by comparison with experimental results we must work out numerical values for particular arrangements of electrons, especially those that are likely to occur in nature. From the theoretical point of view the best examples to choose are the simplest, not only because they easily lead to definite numerical results, capable of experimental verification or otherwise, but also because the fundamental assumptions of the theory, given in §§ 2, 4, 19 and 22 are probably most nearly fulfilled in these cases. Of course, experimental difficulties may arise in realising the conditions needed for a test, such as the production of X- and  $\gamma$ -rays of sufficient intensity within the ranges of wave-length corresponding to the rapid changes of  $\sigma$  occurring near its principal maximum or to the maximum of  $\eta$ . These possible difficulties however do not concern us here, so that we shall choose the comparatively simple cases of helium and lithium as examples. We shall ignore the possibility that all their mobile electrons are arranged in separate rings, for this arrangement is extremely improbable from the theoretical point of view, and in any case would only give values for the scattering coefficients identical with those for hydrogen and therefore needing no further discussion.

26. *Helium.*—We make the usual assumptions  $A = 4, N = n = 2$ . In (39), § 24, there is but one sum, and this reduces to the single term  $i = 1$ ; hence we have

$$\sigma = 0.20 \{1 + f(r)\}, \quad \eta = 0.20 a(r), \quad r = 4\pi\rho/\lambda. \quad (40)$$

There is no need to give graphs, for obviously those given in fig. 2 will serve, if the vertical scale be reduced to one-fifth, and the constant amount 0.20 be added to give the graph of  $\sigma$ .

We see that for very short waves, for which  $f(r)$  vanishes,  $\sigma$  approaches the value 0.20, one-half that of hydrogen, whilst for long waves, for which  $f(r)$  is nearly equal to unity,  $\sigma$  approaches the value 0.40, that of hydrogen. For  $r = 3.1$  or  $\lambda = 4.05\rho$ ,  $\sigma$  is a minimum and equal to 0.209, for  $r = 4.2$  or  $\lambda = 3\rho$ , it is a maximum and equal to 0.215, so that for wave-lengths equal to  $4\rho$  or less  $\sigma$  differs from the simple pulse theory's value 0.20 by  $7\frac{1}{2}$  per cent. at most. On the other hand for  $r = 1$ , or  $\lambda = 12.6\rho$ ,  $\sigma = 0.34$  and differs from its theoretical maximum 0.40 by only 15 per cent.

In order to estimate what these wave-lengths correspond to in absolute measure we must form some idea of the value of  $\rho$ , the radius of the electron

ring of helium. If we take Bohr's theory as a guide and assume that the angular momentum of each electron is  $h/2\pi$ , where  $h$  denotes Planck's constant, we find that  $\rho = 0.303 \text{ \AA.U.}$ , whilst  $\beta$ , the ratio of the velocity of the electrons to that of light, is 0.0127. Thus for the first minimum  $\lambda = 1.23 \text{ \AA.U.}$ , and for the 15 per cent. deficiency below the maximum  $\lambda = 3.82 \text{ \AA.U.}$  Although our theory is quite independent of Bohr's, or any other particular theory of atomic structure, these numbers may serve to give some idea of suitable values of the wave-length for experimental tests. Moreover, since  $r = 4\pi\rho/\lambda = 2\beta v/\omega$ , the corresponding values of  $v/\omega$  are 122 and 39 respectively; these are so large that appreciable vitiation of the results owing to resonance is not to be feared.

Again, as regards the asymmetry, the maximum value of  $\eta$  is 0.064 and occurs for  $r = 2.1$ , or  $\lambda = 6\rho = 1.82 \text{ \AA.U.}$  This value of  $\eta$  corresponds to  $\sigma = 0.238$  and by (38), § 23, gives  $\sigma_e = 0.151$  and  $\sigma_r = 0.087$ , so that the returned is about 58 per cent. of the emergent scattered radiation. Thus the greatest asymmetry is in the direction generally observed and is considerable even for so simple an atom as that of helium. Negative asymmetry is also possible, but it is very small, as we see from fig. 2. Its greatest value corresponds to  $\eta = -0.0044$ ,  $\sigma = 0.214$ ,  $\sigma_e = 0.100$  and  $\sigma_r = 0.104$ , and occurs when  $r = 4.5$ , or  $\lambda = 2.8\rho = 0.84 \text{ \AA.U.}$ ; the corresponding returned is 104 per cent. of the emergent scattered radiation, but the difference is probably too small to be detected by experiment.

27. *Lithium*.—For this element two alternative arrangements of the three mobile electrons in the atom may be suggested: (1) all three in one ring, (2) two in one ring and one by itself in a co-axial ring. In each case we put  $A = 7.06$ ,  $N = 3$ ; further we put  $n = 3$  in (1), and  $n = 2$  for the ring of radius  $\rho$  in (2), the radius of the other ring being immaterial, as its contribution to the scattering coefficients is independent of the wave-length and radius, as with the single electron ring of hydrogen. Thus we obtain from (39), § 24,

$$\left. \begin{aligned} \sigma_1 &= 0.170 \{1 + 2f(r)\}, & \eta_1 &= 0.34h(r), & r &= 2\sqrt{3\pi\rho/\lambda} \\ \sigma_2 &= 0.170 \{1 + \frac{1}{2}f(r)\}, & \eta_2 &= 0.113h(r), & r &= 4\pi\rho/\lambda \end{aligned} \right\}. \quad (41)$$

The graphs given in fig. 2 will again serve, provided that in case (1) we reduce the vertical scale to 0.34 of its value and add the constant amount 0.17 to give  $\sigma$ , whilst in case (2) we reduce the vertical scale to 0.113 of its value and add the same constant amount 0.17 to give  $\sigma$ .

We see that for very short waves  $\sigma = 0.17$ , and  $\eta = 0$  in both cases, in agreement with the simple pulse theory. But for long waves  $\sigma_1$  approaches the maximum value 0.51, considerably greater than the value of  $\sigma$  for

hydrogen, whilst  $\sigma_2$  only approaches the maximum value 0.283, much less than that for hydrogen.

Again, the maximum value of  $\eta_1$  is 0.109, gives  $\sigma = 0.205$ ,  $\sigma_1/\sigma_2 = 31$  per cent., and occurs when  $r = 2.1$  or  $\lambda = 6\rho$ , whilst the maximum value of  $\eta_2$  is only 0.036,  $\sigma = 0.192$ ,  $\sigma_1/\sigma_2 = 68$  per cent., and occurs for  $r = 2.1$  or  $\lambda = 6\rho$ . Thus we see that both the scattering coefficient and maximum asymmetry are so much greater for the first arrangement than for the second that experiment should enable us to decide between them.

In the case of lithium, estimates of wave-lengths are rendered uncertain by the failure of Bohr's theory to provide a satisfactory explanation of the spectrum: nevertheless they are not likely to be so far wrong as to be without value. For the first alternative Bohr's theory gives  $\rho = 0.22$  Å.U.,  $\beta = 0.0176$ , so that the wave-length for maximum asymmetry is 1.14 Å.U., The first minimum of  $\sigma$  is given by  $r = 3.1$ , or  $\lambda = 3.51\rho = 0.77$  Å.U., whilst 15 per cent. deficiency from the maximum corresponds to  $f(r) = 0.775$ ,  $r = 0.866$ , or  $\lambda = 12.6\rho = 2.77$  Å.U. The corresponding values of  $\nu/\omega$  are 140 and 39, so that resonance can hardly be appreciable.

The second alternative is much more uncertain, for we do not know whether the two rings are in the same plane or not, nor do we know which has the greater radius. Consequently we may content ourselves with the rough approximation obtained by neglecting the action of the outer ring on the inner one, and treating the latter as part of the nucleus in estimating its action on the former. Then the radius of the outer ring will be underestimated, that of the inner overestimated, because the repulsion between them is underestimated.

In subcase (a), with the ring of two electrons outside, this ring is practically the helium ring, so that we have  $\rho = 0.303$  Å.U.,  $\beta = 0.0127$ , as in § 26. The maximum asymmetry is given by  $\lambda = 6\rho = 1.82$  Å.U., the first minimum of scattering by  $r = 3.1$ ,  $\lambda = 4.05\rho = 1.23$  Å.U.,  $\nu = 122\omega$ , and the 15 per cent. deficiency below maximum scattering by  $f(r) = 0.625$ ,  $r = 1.165$ ,  $\lambda = 10.7\rho = 3.24$  Å.U.,  $\nu = 46\omega$ .

In subcase (b), with the two-electron ring inside and practically subject to the attraction of three positive charges, we find that  $\rho = 0.19$  Å.U.,  $\beta = 0.0200$ . The maximum asymmetry is given by  $\lambda = 6\rho = 1.14$  Å.U., the first minimum of scattering by  $\lambda = 4.05\rho = 0.77$  Å.U.,  $\nu = 77\omega$ , and the 15 per cent. deficiency below maximum scattering by  $\lambda = 10.7\rho = 2.03$  Å.U.,  $\nu = 29\omega$ .

Thus for lithium the important range of wave-lengths may be regarded as extending from 0.8 Å.U. to 3.2 Å.U., and the values of  $\nu/\omega$  are so great that appreciable vitiation by resonance is hardly likely.

28. The examples of helium and lithium, discussed in §§ 26 and 27, are sufficient to indicate how experiments on the scattering of X- and  $\gamma$ -rays may be used with the twofold object, first, of testing the correctness of the theory of scattering here developed, and with it the truth of the fundamental principles of the electron ring theory on which it is based, and, secondly, of determining the arrangement of the electrons in the atom, if and when the first test has proved satisfactory. It is important to bear in mind that the estimates of wave-lengths given above are only intended to serve as rough guides to the experimenter; their correctness, or otherwise, has no importance for the theory of scattering as such, but can only serve as a test of Bohr's theory of atomic structure. If the theory of scattering survives the test of experiments on the simplest atoms, such as those of hydrogen and helium, further measurements of the scattering by more complex atoms, such as those of lithium, carbon, and so on, will enable us to obtain information respecting the arrangement of the electrons in these atoms. The character of the variation of scattering and asymmetry with the wave-length depends upon the number of rings and the number of electrons in each ring, whilst the position of the maxima and minima depends upon the radii of the rings.

Very few experimental results are available for comparison as yet, and no absolute measurements at all on hydrogen and helium, which are so necessary for a test of the theory. Aurén\* has given a very valuable series of measurements relative to water, from which it appears that the atomic scattering coefficient of lithium is about four times that of hydrogen for  $\lambda = 0.36 \text{ \AA.U.}$  This gives  $\sigma = 0.227$ , with an error which may be as much as 10 or 20 per cent., because of the uncertainty in Aurén's value for the coefficient of hydrogen; for this standard number has to be calculated from water and carbon compounds and necessarily appears as the difference between nearly equal numbers. The value of  $\sigma$  is much greater than the simple pulse theory's value, 0.17, and is well within the limits given in § 27, but it is too unreliable to furnish a reliable estimate for  $\rho$  or to decide between the two arrangements discussed there.

29. We must now consider certain experimental results obtained by Ishino† for very hard  $\gamma$ -rays scattered by aluminium, iron, and lead, bearing in mind that our theory can only be applied to atoms as complex as these with a very rough approximation owing to the comparatively large values of  $\beta$  that are to be expected for some of their rings.

In the first place, Ishino and Madsen before him, found very great asymmetry coupled with a very small scattering coefficient, viz., a ratio

\* 'Phil. Mag.,' Ser. 6, vol. 37, p. 165 (1919).

† 'Phil. Mag.,' Ser. 6, vol. 33, p. 129 (1917).



$\sigma_r : \sigma$ , equal to 0.15 and a mass scattering coefficient of the order 0.04 for aluminium and 0.03 for lead. Thus we obtain for aluminium  $\sigma = 0.04$ ,  $\eta = 0.03$ , and for lead  $\sigma = 0.03$ ,  $\eta = 0.022$ , so that  $\eta$  is about three-quarters of  $\sigma$  for each element. The asymmetry is greater than any we have discussed, but is not so great that it cannot be accounted for by the presence of rings of many electrons. In § 27 we found that a ring of three electrons gave a value of  $\eta$  one-half that of  $\sigma$ , so that a ring of seven electrons, such as Vegard assumes for aluminium, may easily give the requisite asymmetry.

But the smallness of the mass scattering coefficient remains unexplained by the present theory, which gives the simple pulse theory's value as a lower limit. The exceptionally small scattering coefficients observed by Ishino are, however, accompanied by a change of type, a softening of the rays, pointing to an emission of rays accompanying the scattered rays, but of greater wave-length, a fluorescence in other words. May not these be due to *free* vibrations of the electrons, generated by the incident radiation and accompanying the *forced* vibrations to which scattering is due? There is *reason for supposing that some of the free vibrations of the electron rings* are but slightly damped and therefore comparatively persistent, otherwise interference with long path differences would be impossible. Moreover, we know from ordinary dynamics that the initiation of a forced vibration is on the average accompanied by the production of a free vibration, but when the incident vibration is undamped, only a small fraction of its energy is used in generating free vibrations on the average. When, however, the incident vibration is strongly damped, a large fraction of its energy may be used in this way, and a correspondingly smaller fraction scattered. This problem is too long to be discussed here, but is under investigation at present.

#### *The Ring Electron.*

30. Just after the completion of the preceding part of this investigation I became acquainted with the full text of the paper on "The Size and Shape of the Electron," by A. H. Compton,\* in which he considers the scattering of the X- and  $\gamma$ -rays by the flexible ring electron amongst other topics. Evidently this electron may be regarded as the limit of an electron ring when the number of the electrons becomes infinitely great, whilst the total charge and mass remain finite. Hence we should obtain expressions for the scattering coefficients of the ring electron as limiting values of our expressions for the electron ring, especially (25), § 19, and (29), § 21.

For this purpose we suppose  $n$  to become very large and replace  $\epsilon$  by  $\epsilon/n$ ,  $m$  by  $m/n$ ,  $\pi i/n$  by  $\phi$ , and  $1/n$  by  $d\phi/\pi$ . The summations with respect to

\* 'Phys. Rev.,' vol. 14, p. 20 (1919).

$i$  are taken most conveniently from 0 to  $n-1$ , i.e., including the first term, previously separated from the rest, and become integrations with respect to  $\phi$  from 0 to  $\pi$ .

Thus we obtain from (25), § 19,

$$\left. \begin{aligned} \bar{s} &= \frac{e^4}{2\pi c^4 m^2} (1 + \cos^2 \theta) \int_0^\pi \frac{\sin(4\tau \sin \frac{1}{2} \theta \sin \phi)}{4\tau \sin \frac{1}{2} \theta \sin \phi} d\phi \\ &= \frac{e^4}{2c^4 m^2} (1 + \cos^2 \theta) \int_0^1 J_0(4v\tau \sin \frac{1}{2} \theta) dv \\ &= \frac{e^4}{2c^4 m^2} (1 + \cos^2 \theta) \sum_0^\infty (-1)^s \frac{(2\tau \sin \frac{1}{2} \theta)^{2s}}{(s!)^2 (2s+1)} \end{aligned} \right\} \quad (42)$$

where  $\tau = 2\pi\rho/\lambda$  as before.

31. The series represents Compton's ratio  $I/I_{1,0}:I$ , and can be compared with his series (20),\* where  $a$  is used instead of our  $\rho$  for the radius of the ring. The form of the series is the same, but the coefficients are different, on account of a difference in the mode of averaging for the varying orientations of the rings in an assemblage. In our fig. 1, § 7, the pole of the ring,  $z$ , is fixed by its angular distance  $zV$ , or  $\gamma$ , from the fixed point  $V$  and by the angle  $zVU$ , or  $\Omega$ , between the great circle  $zV$  and the fixed great circle  $UV$ ; and we have taken the probability of the orientation  $(\gamma, \Omega)$  to be  $\sin \gamma d\gamma d\Omega/4\pi$ . On the other hand, Compton determines the position of the ring by the angular distance  $TV$ , or  $\alpha$ , from the fixed point  $V$  of the intersection  $T$  of the great circle  $xyT$  (the plane of the ring) with the fixed great circle  $UV$  and by the angle  $yTV$ , or  $\beta$ , between the two great circles; and he takes the probability of the orientation  $(\alpha, \beta)$  to be  $d\alpha d\beta/\pi^2$ . It is easy to prove from the spherical triangle  $zVT$  that  $\sin \gamma d\gamma d\Omega = \sin \beta d\alpha d\beta$ . The difference amounts to this: with us the poles  $z$  of the rings are distributed uniformly over the unit sphere, whilst with Compton the point  $T$  is distributed uniformly over the great circle  $UV$ , and at the same time the plane of the ring  $xOy$  is distributed uniformly about the nodal line  $OT$ . The difference is not, however, of fundamental importance.

32. To obtain  $S(\theta)$ , the whole scattering forwards through a cone of semivertical angle  $\theta$ , we multiply (42), § 30, by  $2\pi \sin \theta d\theta$ , or  $8\pi u du$ , where  $u = \sin \frac{1}{2} \theta$ , and integrate as before. Thus we find

$$S(\theta) = \frac{4\pi e^4}{c^4 m^2} \sum_0^\infty (-1)^s \frac{(2\tau u)^{2s}}{(s!)^2 (2s+1)} \left( \frac{u^2}{s+1} - \frac{2u^4}{s+2} + \frac{2u^6}{s+3} \right). \quad (43)$$

The total scattering is given by  $\theta = \pi$ , or  $u = 1$ ; we obtain

$$S = \frac{8\pi e^4}{3c^4 m^2} \sum_0^\infty (-1)^s \frac{3(s^2 + 3s + 4)(2\tau)^{2s}}{2(s!) (s+3!) (2s+1)}. \quad (44)$$

\* *Loc. cit.*, p. 42.

This can be compared, with Compton's series (21),\* which has the same form as (44), but different coefficients for the reason above assigned.

As regards asymmetry, we obtain Florence's emergent scattered radiation scattered in the forward direction by putting  $\theta = \frac{1}{2}\pi$ , or  $u = \frac{1}{\sqrt{2}}$  in (43); thus we have

$$S(\frac{1}{2}\pi) = \frac{4\pi e^4}{3c^4 m^2} \sum_0^{\infty} (-1)^s \frac{3(s^2 + 5s + 8)(\sqrt{2}\tau)^{2s}}{4(s!) (s+3!) (2s+1)}. \quad (45)$$

The coefficients in the series (44) and (45) are arranged so that the first term is unity in each case; then the coefficient of  $\tau^{2s}$  in (45) is

$$(s^2 + 5s + 8)/(s^2 + 3s + 4) 2^{s+1}$$

times that in (44). It follows that the ratio  $S(\frac{1}{2}\pi):S$ , which is one-half when the frequency vanishes, or  $\tau = 0$ , increases with  $\tau$  to a maximum, and then probably alternates between ever-narrowing limits as the successive terms of the series predominate in turn, in somewhat the same manner as the mass asymmetry coefficients in fig. 2.

33. The series (44) and (45) are convenient when  $\tau$  is small, or  $\lambda/\rho$  large, but for large values of  $\tau$ , or small values of  $\lambda/\rho$ , the computation becomes very laborious owing to the great number of terms required. In this case it is better to use (29), § 21, and (36) § 23, or their equivalents (32), § 22, and (37), § 23. We obtain, by proceeding to the limit for  $n \rightarrow \infty$ , as in § 30,

$$\left. \begin{aligned} S &= \frac{8\pi e^4}{3c^4 m^2} \frac{1}{\pi} \int_0^\pi f\left(\frac{4\pi\rho}{\lambda} \sin\phi\right) d\phi = \frac{8\pi e^4}{3c^4 m^2} \frac{2}{\pi} \int_0^{2\tau} \frac{f(r) dr}{\sqrt{(4\tau^2 - r^2)}} \\ E &= \frac{8\pi e^4}{3c^4 m^2} \frac{1}{\pi} \int_0^\pi h\left(\frac{4\pi\rho}{\lambda} \sin\phi\right) d\phi = \frac{8\pi e^4}{3c^4 m^2} \frac{2}{\pi} \int_0^{2\tau} \frac{h(r) dr}{\sqrt{(4\tau^2 - r^2)}} \end{aligned} \right\}, \quad (46)$$

where  $\tau = 2\pi\rho/\lambda$  as before.  $S$  is, of course, the total scattering coefficient of the ring electron as before, whilst  $E$  is its asymmetry coefficient, defined as in § 23, and equal to the excess of the "emergent scattered radiation,"  $S(\frac{1}{2}\pi)$ , over the "returned scattered radiation,"  $S - S(\frac{1}{2}\pi)$ , each being reckoned per unit intensity of the incident radiation.

A graphic method of computation could be based on the second type of integral by making use of the graphs of the functions  $f(r)$  and  $h(r)$  given in fig. 2, but the vanishing factor  $\sqrt{(4\tau^2 - r^2)}$  would cause difficulties near the upper limit. On the whole, the best method is based on the first type of integral: for a given value of  $\tau$ , or  $2\pi\rho/\lambda$ , the argument  $2\tau \sin\phi$  is calculated for a number of equidistant values of  $\phi$  from 0 to  $\frac{1}{2}\pi$ ; corresponding values of  $f$  and  $h$  are found from the Tables at the end of this paper, and then one of the usual summation formulæ is applied. When

\* *Loc. cit.*, p. 42.

the interval of  $\phi$  is  $\pi/n$ , where  $n$  is an even integer, this amounts to approximately the same thing as calculating  $S$ , or  $E$ , as the case may be, for a ring of  $n$  electrons and dividing the result by  $n^2$ . The greater  $n$  is, the better the approximation will be. Put briefly we may say:

The scattering, or asymmetry, of the ring electron of radius  $\rho$ , charge  $e$  and mass  $m$ , is the limit, when  $n$  is infinitely great, of  $n^{-2}$  times the scattering, or asymmetry, of a ring, of radius  $\rho$ , of  $n$  equidistant electrons of the usual type, each of charge  $e$  and mass  $m$ .

34. The results of most importance for a comparison of the three theories discussed in the preceding pages may be summarised in the following Table, where the total scattering is for convenience sake expressed in terms of  $S_{\text{H}}$ , or  $8\pi e^4/3c^4m^2$ , the total scattering of the hydrogen atom on the simple pulse theory, as a unit.  $N$  denotes the atomic number, taken to be the total number of mobile electrons in the atom, whether ring electrons or electrons of the usual type. For the electron ring theory  $n$ , as before, denotes the number of electrons of the usual type in any one ring, and the sign of summation refers to the several rings, so that  $N = \sum n$ .

Theory.	Maximum total scattering. (Long waves.)	Minimum total scattering. (Short waves.)	Maximum asymmetry.
Simple Pulse . . . . .	$N$ for all wave lengths	$N$	0
Electron Ring . . . . .	$\sum n^2$	$N$	Increasing as $n$ increases.
Ring electron.. . . .	$N$	0	Always large.

The corresponding values of the mass scattering coefficients relative to hydrogen are obtained from those of the relative atomic scattering coefficients given in the second and third columns by dividing by  $A$ , the atomic weight of the element considered.

The Table enables us to indicate experiments which might be crucial in deciding between the several theories. For example, for hydrogen we take  $N = n = 1$ ; according to the simple pulse and electron ring theories the total scattering has the same value unity for all wave-lengths, and there is no asymmetry, but according to the ring electron theory the total scattering only has the value unity for long waves and diminishes to zero for short ones, whilst the maximum asymmetry is as large as that found by Ishino for aluminium, iron, and lead, but probably occurs at a longer wave-length. If the scattering from hydrogen, whether gas under pressure or liquid, can be observed at all, even quite rough measurements should be decisive for or against the ring electron theory, but could not decide between the other two theories.

Again, for helium we may put  $N = n = 2$ ; according to the simple pulse theory the relative total scattering is 2 for all wave-lengths, and there is no asymmetry; according to the electron ring theory the relative total scattering is 4 for very long waves and diminishes to 2 for very short ones, and there is appreciable asymmetry, but much less than that found by Ishino for aluminium and the other metals; lastly, according to the ring electron theory, the relative total scattering is 2 for very long waves and diminishes to zero for very short ones, and there is large asymmetry, comparable with that found by Ishino for aluminium.

Similar results hold for other elements: speaking generally, the simple pulse theory gives relative total scattering equal to the atomic number independently of the wave-length, and no asymmetry; the electron ring theory gives exceptionally large relative scattering for very long waves diminishing to the simple pulse theory's value as a *lower* limit for very short waves, together with appreciable, but relatively small, maximum asymmetry for light atoms and large maximum asymmetry for heavy ones; and lastly, the ring electron theory gives the simple pulse theory's value as an *upper* limit of the relative total scattering for very long waves and values diminishing to zero for very short waves, together with large maximum asymmetry of the same order for all elements, whether light or heavy.

35. The experimental data available for a comparison are few and contradictory.

The relative measurements of Aurén on the total scattering for wave-lengths between 0.34 and 0.38 Å.U. give values much greater than the simple pulse theory's value even for *light* elements, *e.g.*, 0.227 instead of 0.17 for lithium, already mentioned in § 28. Aurén's values include absorption and therefore are subject to vitiation by resonance; but no characteristic radiation of lithium has been observed near his range of wave-lengths, although the J radiation of carbon, originally discovered by Barkla, is not far away. Since 0.17 is the *upper* limit of the total scattering of lithium according to the ring electron theory, this result, as well as others of Aurén, is against that theory, but it is not decisive because the possibility of vitiation by resonance is not excluded.

On the other hand, as we saw in §§ 29 and 35, Ishino found values of the total scattering of aluminium, iron and lead for hard  $\gamma$ -rays of a wave-length about 0.07 Å.U., which were only one-quarter of those to be expected according to the simple pulse theory and also the electron ring theory for very short waves. Compton shows that values of this order are to be expected for a ring electron of radius 0.02 Å.U.; they cannot be explained at all by the simple pulse theory, nor by the electron ring theory developed

above for *light* elements, so long as the  $\gamma$ -rays are regarded as undamped. But two possible explanations may be suggested. In the first place aluminium, iron, and lead are not *light* elements in the sense of the present investigation, in which the effect of the speed of the electrons has been neglected. We have some reason for supposing that some of their mobile electrons move with speeds quite appreciable compared with that of light, so that their mass is greater than  $m$ , that of a slowly moving electron, and the effect of the magnetic field of the incident radiation also must be taken into account. The effect of increase of mass is to diminish the total scattering coefficient; that of the magnetic field requires investigation. Secondly, damping of the incident radiation may be expected to diminish the scattering for the reasons already given in § 29, but the investigation alluded to there, so far as it has gone, shows that it can have no effect in the case of a ring of one electron (hydrogen). It may be urged that damping is irreconcilable with the production of fine spectrum lines, but it should be borne in mind that the resolving power of X-ray spectrographs is far below that of optical instruments, and the phase differences reached are correspondingly smaller, and this seems to be still more true for  $\gamma$ -rays, such as those used by Ishino. Thus an amount of damping would be possible for hard  $\gamma$ -rays, which would be quite out of the question for light. Moreover, it is suggestive that the deficiencies of the total scattering below the simple pulse theory's value observed for carbon and aluminium by Barkla and White\* are very much smaller than those observed by Ishino, commence at wave-lengths from 0.3 to 0.2 Å.U., and increase as the wave-length diminishes. In any case until the investigations on the effects of damping of the incident radiation and of the speed of the electrons have been completed, Ishino's experiments cannot be regarded as decisive against the electron ring theory, although they are strongly in favour of the ring electron theory.

[*Note added December 4.*—The damping investigation has been completed and gives the following results:—For values of  $r$  less than 1.5 slight damping *diminishes* the scattering function  $f(r)$ , but for greater values it *increases* it, but the changes are very small for any admissible amount of damping. Large damping almost certainly diminishes the scattering to the simple pulse theory's value, but not below. Hence damping cannot explain Ishino's low values. The effect of electron speeds comparable with that of light is under consideration.]

36. In order that experiments on scattering should lead to definite theoretical results, the following conditions ought to be approximated to as

\* 'Phil. Mag.,' Ser. 6, vol. 34, p. 270 (1917).

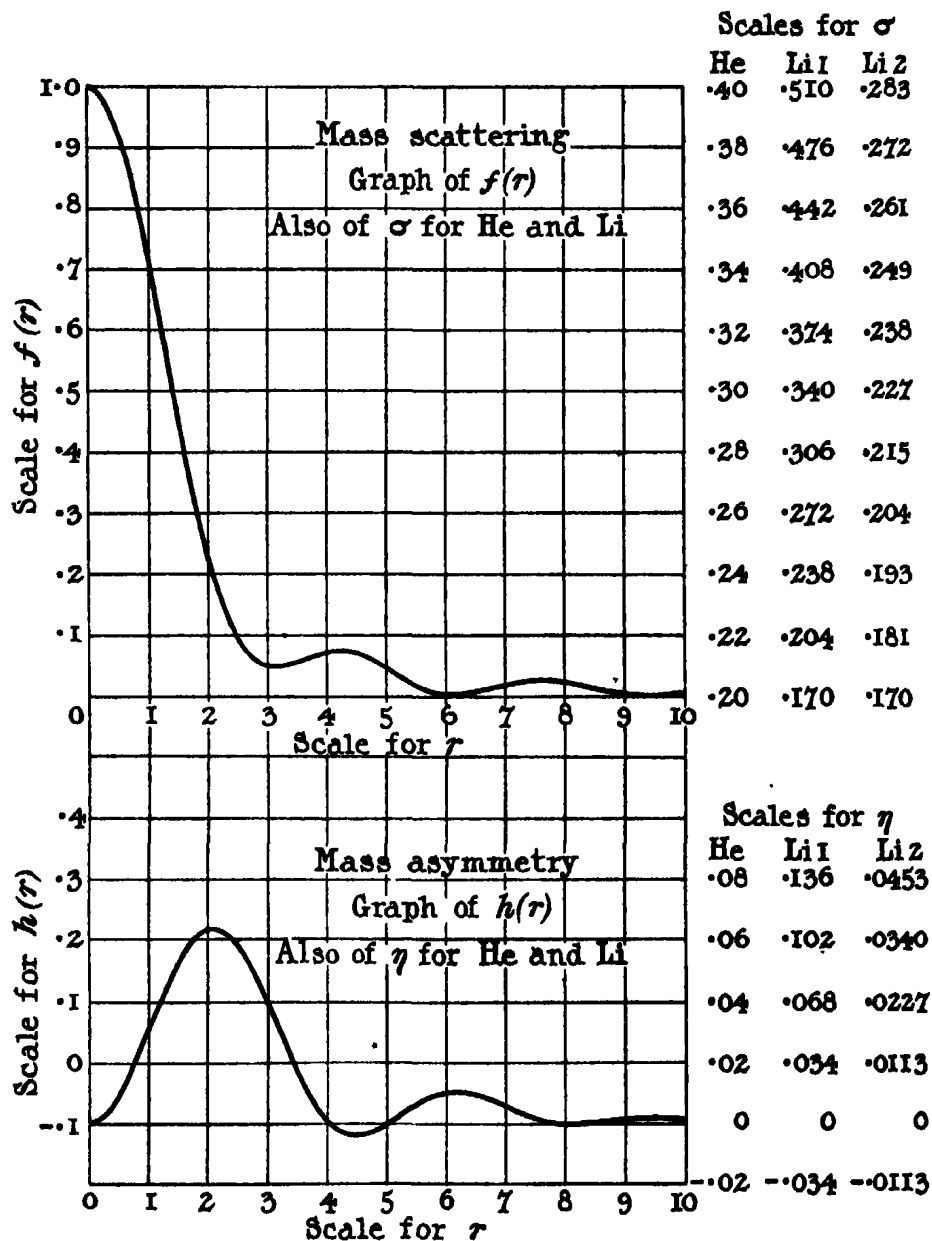


FIG. 2.—Coefficients of He and Li.

nearly as may be consistent with the use of an incident radiation of sufficient intensity to enable measurements of reasonable accuracy to be made: (1) the incident radiation should be monochromatic; (2) the range of

wave-lengths should be wide; (3) the scattered radiation should be sifted from any accompanying resonance or fluorescence radiation of different wave-lengths; (4) contamination of light elements with heavier impurities should be avoided on account of the disproportionate effect of the heavier elements on the scattering for the longer waves.

Experiments on these lines on the absolute scattering in various directions of X- and  $\gamma$ -rays by hydrogen, as well as other light elements, either absolute, or relative to hydrogen, for suitable ranges of wave-lengths, may be expected to give valuable information respecting the nature of the electron, the arrangement of the electrons in light atoms, and the nature of X- and  $\gamma$ -rays,

Tables of the Functions  $f(r)$ ,  $g(r)$ ,  $h(r)$ .

$r$ .	$f(r)$ .	$g(r)$ .	$h(r)$ .	$r$ .	$f(r)$ .	$g(r)$ .	$h(r)$ .
0.2	0.9867	0.0017	0.0068	5.2	0.0388	+0.0020	+0.0111
0.4	0.9479	0.0064	0.0286	5.4	0.0225	0.0068	0.0246
0.6	0.8859	0.0137	0.0624	5.6	0.0131	0.0091	0.0367
0.8	0.8049	0.0228	0.1049	5.8	0.0064	0.0102	0.0454
1.0	0.7100	0.0326	0.1529	6.0	0.0029	0.0100	0.0503
1.2	0.6070	0.0419	0.2008	6.2	0.0023	0.0082	0.0511
1.4	0.5019	0.0497	0.2452	6.4	0.0043	0.0058	0.0484
1.6	0.4003	0.0551	0.2815	6.6	0.0082	0.0024	0.0426
1.8	0.3072	0.0575	0.3063	6.8	0.0180	-0.0006	0.0344
2.0	0.2264	0.0564	0.3183	7.0	0.0178	-0.0033	0.0262
2.2	0.1604	0.0518	0.3163	7.2	0.0218	-0.0055	0.0178
2.4	0.1108	0.0443	0.2990	7.4	0.0244	-0.0066	0.0102
2.6	0.0758	0.0344	0.2728	7.6	0.0252	-0.0066	0.0045
2.8	0.0554	0.0231	0.2353	7.8	0.0241	-0.0058	0.0010
3.0	0.0468	0.0114	0.1921	8.0	0.0215	-0.0042	-0.0008
3.2	0.0470	0.0022	0.1462	8.2	0.0176	-0.0022	-0.0010
3.4	0.0526	-0.0095	0.1011	8.4	0.0132	-0.0001	+0.0007
3.6	0.0607	-0.0169	0.0598	8.6	0.0088	+0.0019	0.0028
3.8	0.0685	-0.0218	0.0252	8.8	0.0049	0.0038	0.0055
4.0	0.0740	-0.0235	0.0016	9.0	0.0022	0.0042	0.0080
4.2	0.0757	-0.0228	-0.0149	9.2	0.0007	0.0044	0.0095
4.4	0.0733	-0.0196	-0.0219	9.4	0.0005	0.0042	0.0104
4.6	0.0689	-0.0150	-0.0201	9.6	0.0016	0.0029	0.0108
4.8	0.0674	-0.0098	-0.0141	9.8	0.0035	0.0015	0.0105
5.0	0.0459	-0.0084	-0.0025	10.0	0.0060	0.0000	0.0093

In conclusion, I wish to thank Prof. Sir J. Larmor for his interest in the work, and his valuable criticisms and suggestions.



## *A Note on Dr. Chree's Recent Discussion of Two Magnetic Storms.*

By S. CHAPMAN, M.A., D.Sc., F.R.S., Professor of Mathematics and Natural Philosophy in the University of Manchester.

(Received November 1, 1919.)

In 'Proceedings,' Ser. A, vol. 96, pp. 32-55, Dr. Chree describes certain records of two great magnetic storms which occurred in 1918, and in connection with them adverts frequently to various portions of a paper\* of my own, entitled "An Outline of a Theory of Magnetic Storms." On p. 32 he states that the two storms are of the kind discussed in my paper (and to this I agree), but that the results differ much from those which I gave as representative of world-wide magnetic storms. No precise summary of the alleged differences was given, and the only ones to which attention was expressly drawn seem to be as follows: (a)† the initial sudden rise in the value of  $H$  (horizontal force), as shown in fig. 1 of his paper, is much less, proportionately, than in the corresponding curve in my fig. 1; and (b)‡ while the Kew and Eskdalemuir  $H$  diagrams for March 7-8 resemble my fig. 1, "it is otherwise" with the Agincourt  $H$  diagram for the first part of the storm.

As regards (a), my fig. 6, illustrating how the changes in  $H$  depend on the intensity of the storm, shows that the greater the storm the less is the ratio borne by the initial rise in  $H$  to the subsequent fall. As Dr. Chree's storms are much more intense than those illustrated in my fig. 1 the difference he notes is in accordance with my results.§

As to (b), it is to be observed that Dr. Chree is comparing different things when he places the curves of his and my fig. 1 alongside each other. In my paper I stated that the variation of  $H$  (or other magnetic element) at any station during a storm was composed of three parts, which I termed the storm-time, the local-time, and the irregular variations. To derive

\* 'Roy. Soc. Proc.,' A, vol. 95, pp. 61-83.

† *Loc. cit.*, p. 37.

‡ *Loc. cit.*, p. 39.

§ In connection with the influence of intensity on the course of a magnetic storm, Dr. Chree (p. 39) refers to the acceleration of minimum phase with increasing intensity, which was noted in my paper. He supposes me to have concluded that this acceleration is small, otherwise I "would hardly have derived (my) results, as one infers (I) did, from the superposition of storms irrespective of size." My fig. 6, on the contrary, clearly indicates considerable acceleration; and my storms, both those of fig. 6 and of those of fig. 1, were carefully grouped according to size.

the two former, regular, variations, I averaged the results (in two different ways), from a number of similar storms, thus eliminating most of the accidental variations. My fig. 1 illustrates only the resulting storm-time variations, the local-time variations being given in figs. 3-5; Dr. Chree's fig. 1 includes all three parts of the variation. It is not to be expected that, by mere inspection of the records of two or three stations for a single storm, one should be able to disentangle the three parts of the whole variation, and so to test whether these parts are conformable with my results.

In the given case, however, the difference (*b*) indicated by Dr. Chree does not appear to conflict with those representative types. If the difference were part of the accidental variation—a quantity which cannot be predicted beforehand, nor recognized with certainty (unless possibly from the results of many stations taken together) when present—nothing more need be said. But it seems likely that in the given case the irregular variation is small; the difference should then, according to my paper, be due to the presence of the local-time variation in Dr. Chree's, but not in my, fig. 1. Dr. Chree mentions that this might be alleged as the reason, but rejects the explanation because the local-time variation in *H* at Kew and other European stations is small. I agree that the latter is the fact, and see therein the cause of the similarity between the Kew *H*-curves and my own; the local-time variation being small, its presence does not destroy the resemblance with my curve, from which it is absent. At Agincourt, on the contrary, the local-time variation in *H* is not small,\* and has a large maximum at about 18 h. local time; to this I attribute the presence of the positive peak in Dr. Chree's Agincourt curve (fig. 1) at about 21 h. local time.

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\* The evidence for this will be given in a future discussion of the local-time variation at a number of observatories spread widely over the Northern hemisphere. Cf. also fig. 3, section 1*b*, of my paper.

*An Explanation of Criticisms on Dr. S. Chapman's Recent Paper, "An Outline of a Theory of Magnetic Storms."*

By C. CHREE, Sc.D., LL.D., F.R.S.

(Received November 20, 1919.)

Criticism of Dr. Chapman was not the primary object of my paper,\* and it would seem that I have studied brevity too much in referring to differences which to myself were conspicuous. That fault I shall hope to repair now. But first I should make it clear that there are certain points about which there is, I think, no difference of opinion. Our knowledge of magnetic storm phenomena in high latitudes is very limited, but in low and moderate latitudes the following phenomena in the variations of  $H$  (horizontal force) during storms having  $Sc$ 's (sudden commencements) have been, I think, generally recognised for many years. The result of the  $Sc$  movement or movements is almost invariably to enhance  $H$ , and a marked fall does not as a rule set in immediately.

This rule is not absolutely without exception. For instance, on the occasion of the very large storm on August 11-12 of the present year, a large reverse movement set in so soon after the  $Sc$  that the mean values alike for the first hour, the first half hour, and even the first quarter hour of "storm time" are much below the pre-storm value. Still exceptions are rare, and the mean value of  $H$  for the first hour or half hour after the  $Sc$  is nearly always in excess of the pre-storm value.

*Sooner or later* a marked fall sets in, which, though generally interrupted by oscillations, usually reduces the value of  $H$  well below the pre-storm value, and again *sooner or later* this is followed by a recovery, which in its turn may be interrupted by oscillations.

So far, I think, there is pretty general agreement. The doubtful points are essentially two: 1st. Is the sequence of events after the  $Sc$  so uniform as to make the general use of "storm time" desirable? 2nd. Are the phenomena at stations so dominated by the distance from the earth's magnetic axis that Dr. Chapman's combination of them into groups, determined by that distance, is really helpful?

As I carefully pointed out, I had selected the two storms discussed in my paper before Dr. Chapman's paper appeared. But, *as it so happened*, they brought up the two doubtful points in an acute form. The Kew and Eskdalemuir  $H$  curves for March 7-8, as Dr. Chapman remarks, do show a

\* 'Roy. Soc. Proc.,' A, vol. 93, p. 32.

considerable general resemblance to the corresponding curve of his fig. 1; but side by side with these in my fig. 1 are the corresponding curves for August 15-16—which seem to have escaped Dr. Chapman's eye—and in these H continued to rise for several hours after the Sc. This seemed, and still seems to me, a notable difference.

The second point was raised by the Agincourt H curve for March 7-8 which also appeared in my fig. 1. In this case it will, I think, be well to glance at the size of the differences between Agincourt on the one hand, and Kew and Eskdalemuir on the other, as given for H in my Table I.\* The algebraic excess of the Agincourt departure from the pre-storm value over the Kew departure was 130  $\gamma$  at 1.5 h. on March 8, and more than 340  $\gamma$  at 2.5 h. The corresponding algebraic excesses of Agincourt over Eskdalemuir were respectively 292  $\gamma$  at 1.5 h., and more than 532  $\gamma$  at 2.5 h. The differences we have to explain are thus enormous. Dr. Chapman is now apparently disposed to ascribe them to a large "local time" variation at Agincourt, since, as he admits, the local time variation at the European stations is not large. Apart from the gigantic variation required, I do not see how Dr. Chapman can possibly reconcile this with the fundamental assumptions of his first paper. According to it the "local time" variation, equally with the "general storm" variation, should have been determined simply by the distance of the station from the Earth's magnetic axis. Its amplitude should thus have been practically identical for Kew and Agincourt—these two stations having, as I pointed out, the same magnetic latitude—the only difference being five hours in the phase angle. The amplitude as shown by the curve 3b in Dr. Chapman's fig. 3 is only about 20  $\gamma$ .

I may add that, in connection with the discussion of the Scott Antarctic Expedition magnetic data of 1911-12, I have had occasion to compare a large number of disturbances at Agincourt with corresponding disturbances at Eskdalemuir and Kew. These suffice to show that Agincourt is in general a much more highly disturbed station than Kew. This is one of my reasons for thinking that the classification of stations according to distance from the magnetic axis is not well advised.

The criticism that he had derived his results from storms, irrespective of size, which Dr. Chapman quotes from my p. 39, referred to his fig. 1. In the case of his fig. 6, which was restricted to two stations, Bombay and Pavlovsk, storms were presented in three groups according to size. With only three groups there would naturally be a considerable range of amplitude within any one group, still a distinction was made. But fig. 1, unlike fig. 6, shows only one set of curves for each group of stations. I had supposed that,

\* *Loc. cit.*, p. 35.

except for Bombay and Pavlovsk, Dr. Chapman had confined himself to forty storms of "considerable, though not outstanding intensity,"\* and that his figs. 1, 3, 4, and 5, represented results derived from superposing all these, irrespective of size or duration. If the storms were specially selected, the criteria observed should certainly have been explicitly stated, and corresponding reservations made in presenting the conclusions as universally applicable.

The storms considered in my paper were moderate ones. They were trifling for instance, as recorded at Kew, compared with the recent storm of August 11-12. But without knowing more of the storms on which Dr. Chapman based his fig. 1, I cannot say how much of truth there may be in the explanation which he gives of the comparative shallowness of the depression of H shown by that figure. A different explanation occurs to me. The time subsequent to a Sc when a marked fall appears in H, even in storms of similar size at the same station, is in my experience a very variable quantity. Similarly, the time when a marked recovery sets in is highly variable. Thus, when one superposes, following "storm time," a large number of H curves, the only feature that is universal, or nearly so, is the enhancement immediately following the Sc. After the first hour or half hour of "storm time" positive contributions from some storms are superposed on negative contributions from others. Thus the maximum depression apparent in the composite curve is small compared with the arithmetic mean of the depressions in the individual curves.

\* *Loc. cit.*, pp. 63 and 64.

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## *The Measurement of Magnetic Susceptibilities of Low Order.*

By ERNEST WILSON, M. Inst. C.E., M.I.E.E., Siemens Professor of  
Electrical Engineering in the University of London.

(Communicated by Prof. J. W. Nicholson, F.R.S. Received September 3, 1918.)

### *1. Introductory.*

The magnetic susceptibilities of various kinds of rock specimens have recently assumed considerable importance in relation to the new magnetic survey of the British Isles, and in this connection as a member of the Iron Ore Committee of the Conjoint Board of Scientific Studies, the author was asked to endeavour to obtain a solution of the problem, which, in its essentials, consisted mainly in the development of some instrument capable of measurement of susceptibilities of low order. At the suggestion of the Committee the author has prepared the present communication which contains an account of the instrument used, together with some of the results to which it has led. The particular work on rock specimens which was the origin of the enquiry is given in "A Report on Magnetic Disturbances in Northamptonshire and Leicestershire and their Relation to the Geological Structure."\*

The type of instrument which has been used in the work described in the present communication is a modification of that known as the Curie balance,† and depends for its action upon the pull exerted by a magnet.

### *2. The Magnetic Circuit.*

The core of the magnetic circuit is in the form of a ring cut from a plate of a 3 per cent. silicon alloy of iron known by the name of Stalloy. This material was chosen because of its high permeability at low values of the magnetic force. The ring has an outside diameter of 18 cm. and an inside diameter of 10·5 cm. Its thickness is 1·6 cm. An air-space with parallel sides is cut in the ring and its width is 1·5 cm. The poles are tapered at an angle of 60° with the plane of the ring, and the opposing faces are 1 cm. wide. The ring is wound up to the pole pieces with five layers of copper wire of diameter 0·122 cm., insulated with two layers of cotton. The numbers of turns on the layers from innermost to outermost are 184, 182, 176, 170, 161—total 873.

\* 'Phil. Trans.,' A, vol. 219 (1919), Appendix.

† 'Annales de Chimie et de Physique,' 7e Série, vol. 5 (1895); 'Journal de Physique,' 4e Série, vol. 2 (1903); 'Proc. Phys. Soc.,' London, vol. 22, pt. 3, pp. 342-356.

The calculated ratio of the force in the air-space without the inserted specimen to the magnetising current in amperes varies from 676 to 725 owing to the changing permeability of the stalloy as the force in the air-space varies from 8 to 1000 C.G.S. units. This is in close agreement with experiments made with an exploring coil inserted in the air-space and a ballistic galvanometer.

### 3. *Description of the Instrument and Apparatus.*

The electromagnet M (fig. 1) which produces the magnetic field is supported in a vertical plane on a wooden base which is capable of motion to and fro

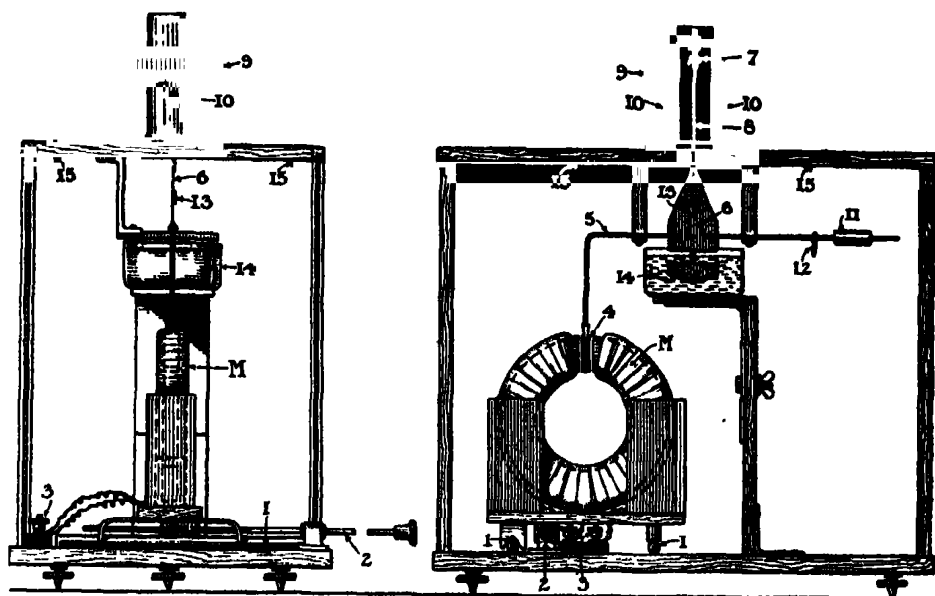


FIG. 1.

on brass rails, 1, 1, of circular section. The movement is controlled by a screw, 2, having 20 threads to the inch which is turned by hand. The winding on the electromagnet is continued by flexible conductors to terminals, 3, fixed on the base at the back of the instrument. The specimen, 4, whose susceptibility is required is supported in a grip made of thin sheet aluminium or tin, which forms the extremity of a beam, 5, made of aluminium wire 0.32 cm. diameter. The horizontal distance between the centre of the vertical portion of the beam and the centre of suspension is 10.9 cm. which is therefore the effective radius. The horizontal portion of the beam passes through a piece of sheet aluminium, 6, which is suspended from the head-piece, 7, by a phosphor-bronze strip, 8. The strip is 10 cm. long and of rect-

angular section 0.85 mm.  $\times$  0.09 mm.\* The head-piece consists of two concentric tubes of brass, the outer one being fixed to the frame work, and the inner one capable of being raised or lowered by a ring, 9, which has a screwed thread on the inside, and engages the thread cut on the outer surface of the inner tube. Two screws, 10, 10, fixed to the inner tube and working in vertical slots in the outer tube prevent the inner tube from rotating. The specimen is counterbalanced by an aluminium sliding weight, 11, and an aluminium rider, 12. The mirror, 13, is fixed to the aluminium sheet which supports the horizontal beam, 5, and the moving system is damped by submerging an extension of it in an oil bath, 14. In order that the strip, 8, may be maintained in a vertical position, four sighting pins, 15, are so arranged that the intersection of the two straight lines joining obliquely opposite pins coincides with the true centre of suspension. The instrument is closed in at front and back by sheet glass which is capable of being moved upwards or downwards after the manner of an ordinary chemical balance.

A storage cell battery is employed to supply the magnetising current which is measured on an ampère meter. An adjustable resistance is included in the circuit in order that the magnetising current can be conveniently adjusted to produce the required magnetising force  $H$  in the air-space of the electromagnet. A reversing switch is employed primarily for the purpose of demagnetising the magnet by reversals when variations in the force  $H$  are required, and for removing all traces of residual magnetism.

#### 4. The Field of the Electromagnet.

Preliminary experiments were made before deciding upon the shape of the pole-pieces, and much was already known in this connection from an investigation by Nagaoka,† who has examined the distribution of the magnetic field in the neighbourhood of differently shaped pole-pieces by aid of the variation of Zeeman effect at different points of the field. Unfortunately this method ceases to be applicable when fields so low as 3000 C.G.S. units are employed on account of diminished sensibility.

M. P. Curie (*loc. cit.*), in his original apparatus, employs two equal cylinders of iron with their circular ends as pole-pieces. The axes of these cylinders are in a horizontal plane, and inclined at an angle of about  $144^\circ$ , the distance between the nearest points being equal to the diameter of either cylinder. Each cylinder is wound with a magnetising coil, and the magnetic circuit is

\* For greater sensitivity a phosphor-bronze strip of rectangular section, 0.85 mm.  $\times$  0.04 mm. has been employed.

† 'Tôkyô Sôgaku-Buturigakkwai Kîzi,' 2nd Ser., vol. 8, No. 3, p. 73.



completed by yoke-pieces screwed to the base-plate. Regarding the axis of  $x$  as the direction in the horizontal plane bisecting the angle of inclination of the axes of the cylinders, and the direction at right-angles to this as axis of  $y$ , it was necessary to find the value of  $dH_y/dx$  where  $H_y$  is the magnetic intensity at right-angles to  $x$ . A circular search coil was placed in the  $x$  axis with its plane normal to the magnetic field, and on moving it quickly from point to point in the direction  $x$  a series of deflections of a ballistic galvanometer was observed, from which  $dH_y/dx$  could be found. On account of irregularities it was found preferable to employ a different method based on the fact that  $dH_y/dx = dH_z/dy$ , a necessary property, of course, of any magnetic field arising from a magnetic potential. The search coil was therefore placed with its plane parallel to the direction of the field and normal to the direction  $x$ , the displacements being in the direction  $y$ .

In the present experiments a new method for the exploration of the field in the air space has been devised, which depends not on the determination of  $dH_y/dx$ , but on the direct measurement of  $dH_z/dy$ . It is therefore in some respects essentially different; and it is of course evident that the modification of the Curie balance, which admits such a direct measurement, must possess considerable practical advantages.

The arrangement is shown in fig. 2. A fine straight wire of platinum,  $p$ , 4 cm. long, was fixed vertically to the extremities of two parallel aluminium wires,  $a$ , lying in horizontal planes 4 cm. apart. The aluminium wires were fixed to a rod of ebonite,  $c$ , which hung vertically, and was attached by a vertical conductor,  $e$ , to the phosphor bronze suspension, whose force of torsion it was required to measure. Looking at the aluminium wires in a direction normal to the horizontal planes, the two extremities above mentioned are centrally situated between the poles of the magnet,  $M$ , and in the mid-plane of the magnet ring. The wires from these points are straight for a distance of 5.5 cm. in a direction normal to the plane of the ring, the object being to confine the force to the vertical platinum wire. They then curve round towards the centre of suspension of the instrument, where they are attached to the vertical ebonite support. In this manner the platinum wire,  $p$ , is capable of movement in a direction at right angles to its length, and for small arcs at right angles to the plane of the magnet ring. A small mirror,  $m$ , was attached to the axis of this moving system, and in conjunction with a spot of light and scale was used to measure the angular displacements. An electric current was passed through the vertical platinum wire,  $p$ , in the following manner. A storage cell had its positive pole connected through an ampère meter and an adjustable resistance to the head-piece of the instrument. The current could then flow through the phosphor bronze

strip to the upper of the two horizontal aluminium wires. It then passed along this wire to the platinum wire, *p*, and thence to the lower aluminium wire back to the centre of support. It could then flow down a vertical conductor, *d*, dipping into mercury, Hg, which was connected with the negative pole of the cell. For the purpose of speedily bringing the moving system to

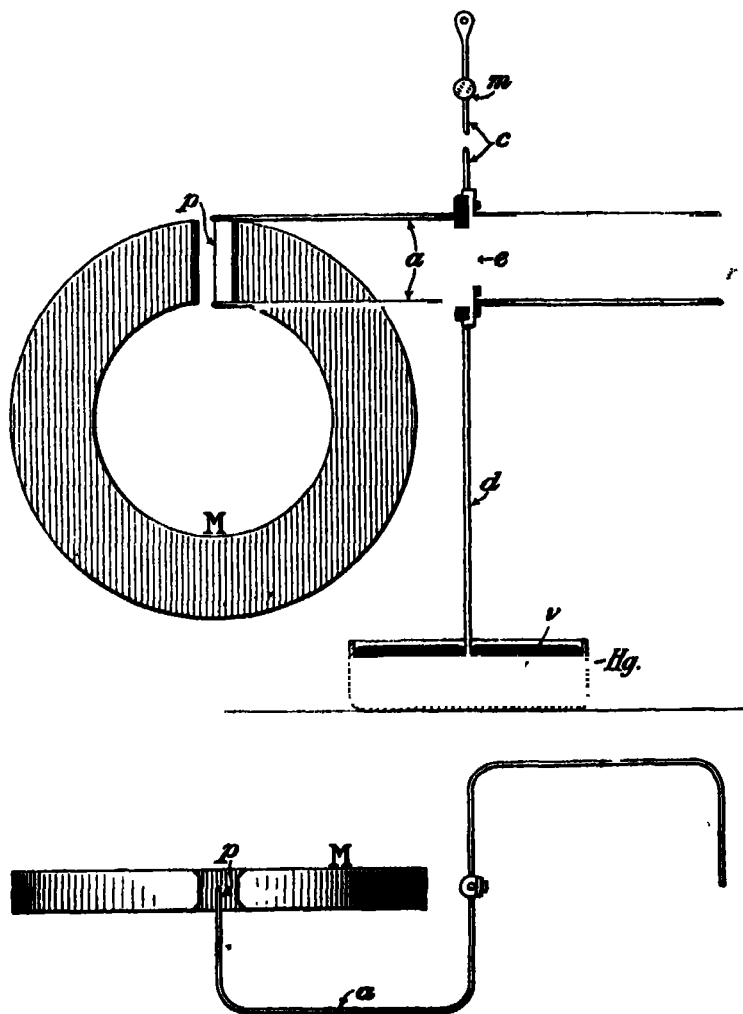


FIG. 2.

rest, a vane, *v*, of platinum foil attached to the system was submerged in the mercury.

When it was desired to measure the variation of the strength of the magnetic field of the magnet in a direction  $Ox$  at right angles to the plane of the magnet ring, an electric current, *a*, was caused to flow through the

vertical wire,  $p$ , and was maintained constant. The magnet was excited by a current,  $A$ , and the deflection  $+\theta$  was noted. The current  $A$  was then reversed in sign and the deflection  $-\theta$  noted. The current  $A$  was then broken, and the magnet was moved forward by turning the adjusting screw through one revolution. This produced a movement of 0.127 cm. In this way a series of observations was made, which rendered it possible to determine graphically the variation of the force exerted by the magnet in terms of the distance  $Ox$  from the central point of the air-space at right-angles to the plane of the ring.

#### 5. *Force on the Suspended System.*

If the intensity of the magnetic field is constant and equal to  $H$ , then the mechanical force in dynes which, acting on the vertical conductor, produces 1 degree of twist is equal to

$$Hla/\theta \times \text{constant};$$

where  $l$  is the length of the conductor,  $a$  the current in the conductor, and  $\theta$  the observed deflection. A number of determinations were made, and they indicate a mean value of 1.51 dynes per degree of twist.

A further test was made by suspending a horizontal bar of known moment of inertia, and observing its time of oscillation. The details of these observations are not included, as they follow obvious lines. The value of the force in dynes for 1 degree of twist at this radius is for a large bar 1.516. For a small bar the force is 1.487 dynes. The average value obtained from these determinations is 1.50 dynes, which is in close agreement with the value 1.51 found by the electrical method.

#### 6. *Field of the Vertical Conductor.*

A possible disturbing factor which requires examination is the magnetic effect of the current,  $a$ , in the vertical conductor. This current was varied for the same strength of the magnetic force,  $H$ , in the air-gap. Conversely for the same value of  $a$  the magnetising force,  $H$ , was varied. The constancy of the results and their agreement with those of the mechanical tests indicate that when the vertical conductor is within the air-gap the disturbance caused by the current is under the conditions of the experiments inappreciable. The effect of susceptibility of the platinum wire was investigated separately.

#### 7. *On the Relation between Magnetic Force of Excitation and Magnetic Susceptibility.*

Some light is thrown upon certain effects which have been observed during the course of the present experiments by a study of the magnetic properties

of iron filings which were tested by the author by the ballistic galvanometer ring method before and after heating to 900° C.\* The curves showing the relation found in this way between the magnetic induction, B, and the magnetic force, H, do not deviate greatly from straight lines for values of H up to 150 C.G.S. units or more, and they indicate average values of the susceptibility 0.54 and 0.79 respectively. In the present experiments on certain of the rock specimens in connection with the Geological Survey, the relation between the magnetic force, H, and the susceptibility is very nearly a straight line. For example, with the partially oxidised oolitic ore (N.88) the following results were obtained, and they illustrate a very close approximation:—

H ø/Å <sup>2</sup> V	44 2500	67 2460	100 2564	200 2585
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In the case of igneous rocks of high susceptibility there are indications of a maximum susceptibility at the intermediate forces.† The following figures were obtained for example, with dolerite from Whitwick, Leicestershire (L 114), normal granite, Mount Sorrel Quarry, Leicestershire (L 15), and augite-granophyre (syenite), from Groby Quarry, Charnwood Forest (L 13).

	L 114 (high).		L 15 (fairly high).		L 13 (low).		
H .....	23	39	47	69	96	200	335
ø/Å <sup>2</sup> V .....	33,200	38,200	5490	5490	6070	356	345

### 8. The Instrumental Constant.

It has been shown that when the susceptibility of the specimen (K) does not exceed 0.01 C.G.S. units, the magnetic force, H, in the air space is proportional very nearly to the current in the magnetising coil. Let the current in amperes be denoted by A so that  $H \propto A$ . H is also a function of  $x$ , the distance measured at right angles to the plane of the magnet ring from a point midway between the pole pieces, and lying in the mean plane of the ring. Let this function be denoted by  $f(x)$ . We have then  $H = qA f(x)$  where  $q$  depends neither on the amperes A, nor the distance  $x$ . Then if V is the volume of the body the mechanical force, F, exerted by the magnetic field upon the specimen is given by

$$F = \frac{1}{2}KV \frac{d}{dx} \{q^2 A^2 f^2(x)\} = \frac{1}{2}KV q^2 A^2 \frac{d}{dx} f^2(x).$$

\* 'The Electrician,' October 5, 1900.

† Compare Rücker, 'Roy. Soc. Proc.,' vol. 48, p. 505 (1900).

Therefore, for any given distance,  $F\alpha A^2$ , and since the observed deflection  $\theta$  is proportional to  $F$ , we have  $\theta$  proportional to  $A^2$ , or  $\sqrt{\theta\alpha A}$ . It follows that for unit volume the absolute value of the susceptibility,  $K$ , is equal to the observed deflection,  $\theta$ , divided by the square of the current in amperes and multiplied by a constant peculiar to the instrument. That is to say  $K = C\theta/A^2V$ ; where  $C$  will be called the instrumental constant. The determination of this constant is naturally the fundamental problem for any instrument constructed after this pattern. It has been performed in various ways, only a few of which are indicated in the succeeding sections.

### 9. *Mode of Determination of the Constant with Specified Material.*

Five determinations of the instrumental constant have been made in which the intensity of the magnetic force in the air-space was varied from 221 to 2210 C.G.S. units. In any one experiment the average values of the observed deflections  $+\theta$  and  $-\theta$  have been plotted in terms of the distance  $Ox$  at right angles to the plane of the magnet ring, and, from the curve so obtained, the values of the magnetic force  $H$  in arbitrary units have been taken.

Let  $H_0, H_1, H_2, \dots$  be consecutive values of the magnetic force due to the magnet along the line  $Ox$ , separated by intervals  $\delta x$ . It is required to find the average value of  $H \frac{\partial H}{\partial x}$  over a distance along  $Ox$ , covered by the specimen when the maximum deflection is obtained. The value of  $\delta x$  adopted in the experiments is 0.127 cm., and, if the specimen has a width along  $Ox$  of 1 cm., we may take it that the area of the curve included between ordinates separated by 1 cm., which give a maximum value, will approximately determine the equilibrium position of the specimen. Since at any point between the extreme positions, supposed close together, defined by the suffixes zero to unity,

$$H \frac{\partial H}{\partial x} = \frac{H_0 + H_1}{2} \times \frac{H_0 - H_1}{\delta x} = \frac{H_0^2 - H_1^2}{2\delta x},$$

it is necessary to square the values of  $H_0, H_1, H_2, \dots$ , take the difference of successive pairs of these, and divide by  $2 \times 0.127 = 0.254$  in determining the value of  $H \frac{\partial H}{\partial x}$  between these pairs.

The values of  $H_0, H_1, H_2, \dots$  in arbitrary units have been taken, and the mean curves plotted from the average deflections, as already described. It is found, by direct measurement of areas, for example, when  $H$  max. is equal to 469 C.G.S. units, as in Experiment No. 2, that the mean value of  $H_2^2 - H_1^2$ , etc., or  $\partial(H^2)$  between  $x = 1$  and  $x = 9$  inclusive, is 332; and the

mean value between  $x = 2$  and  $x = 10$  inclusive is 330. The specimen will, when the deflection is a maximum, be nearly symmetrical with the ordinate at the point defined by  $Ox = 5.5$ . A constant of the instrument will now be worked out, making use of the mean value 332 thus obtained. The scale used in the experiments is divided into 1000 equal divisions, counting from the extreme left, and it is curved to the radius of the spot of light. A maximum deflection is obtained in the first place by moving the magnet in one direction from its mean or central position, and then by moving it in the opposite direction. Thus the difference between the two readings gives double deflections, which are an ultimate measure of the susceptibility. If  $K$  is the volume-susceptibility in C.G.S. units,  $\theta$  the observed deflection in double scale divisions,  $A$  the magnetising current in amperes, and  $V$  the volume of the specimen in cubic centimetres, then the instrumental constant  $C$  for small values of  $K$  is equal to  $KA^2V/\theta$ . One double deflection corresponds to a single deflection from the mean position of one half-division, or  $1/40$  cm. The scale is distant 77 cm., and therefore the angle of twist  $= 0.0093^\circ$  if allowance is made for the deflection being doubled by the reflection of light.

The mechanical force in dynes per degree of twist is 1.52, so the total mechanical force is  $1.52 \times 0.0093 = 0.0141$  in this instance. The maximum value of the magnetic force  $H$  in the gap is 670 C.G.S. units for a value of  $A$  of 1 ampère. Thus  $H^2 \text{ max.} = 450,000$ , and the instrumental constant

$$C = \frac{0.0141 \times (63.5)^2 \times 0.254}{332 \times 450,000} = 96.9 \times 10^{-9}.$$

A summary of the results obtained in the five determinations is given in the following Table, and the mean value of the instrumental constant is  $93.6 \times 10^{-9}$ .

Experiment.	Magnetising current $A$ .	Maximum magnetic force in the air-space.		Current in vertical conductor $a$ .	Mean value of $d(H^2)$ in arbitrary units.	Instrumental constant $C$ , $10^{-9}$ .
		Arbitrary units.	C.G.S. units.			
1	0.33	29.5	221	ampères. 0.00957	76	91.8
2	0.70	63.5	469	0.00957	332	96.9
3	1.02	59.5	693	0.00859	311	90.8
4	2.01	66.0	1460	0.00890	392	94.0
5	3.06	68.5	2210	0.00280	395	94.8
Mean .....						93.6

10. *Effect of Finite Size of the Specimen.*

The above value of the instrumental constant  $C$  strictly requires a further connection as no account has been taken hitherto of the fact that the specimen has an approximately circular cross-section of finite size. Assuming that the lines of force in the specimen are straight lines parallel to the plane of the magnet ring, the mechanical force on an element of volume  $dV$  is  $KdVH\frac{\partial H}{\partial x}$ . Take as the element a slice of breadth  $dx$ , width  $2y$ , and height 1 cm., and the force on the element is

$$\delta F = 2KyH\frac{\partial H}{\partial x}\delta x.$$

The total force for the specimen is accordingly

$$F = \int_{x_1}^{x_2} 2KyH\frac{\partial H}{\partial x}\delta x.$$

For a cylindrical specimen of radius  $R$

$$y = \sqrt{R^2 - (x - x_1)^2}.$$

Therefore 
$$F = 2K \int_{x_1}^{x_1+2R} H \frac{\partial H}{\partial x} \sqrt{R^2 - (x - x_1 - R)^2} dx;$$

where  $R$  is the radius of cross-section. This can be evaluated by quadrature in a given number of equal parts, but after evaluating it analytically by this method, on the assumption that the graph of  $H\frac{\partial H}{\partial x}$  against  $x$  was approximately parabolic, and again, by direct measurements from a completely graphical treatment, it was found that the latter method was much more satisfactory. In fact, the curve is not sufficiently parabolic to render any analytical treatment of greater value, for it is unsymmetrical on the two sides of its vertex.

The actual method adopted was therefore the construction of a graph of the integrand in the preceding formula, and the evaluation of the integral between any limits by direct measurement of the area included between this graph and the corresponding ordinates.

11. *Determination of Constant by Use of Iron Ores and Alloys.*

(a) *A 13 per cent. Alloy of Manganese and Iron.*—A ring of this alloy, given to the author many years ago by Sir R. A. Hadfield, F.R.S., having an internal diameter of 5.25 cm., and an external diameter of 7.3 cm., and a depth of 3.5 cm., was tested with the ballistic galvanometer. Its permeability was found to be 1.3 ( $K = 0.0239$ ) for forces  $H$  up to about

200 C.G.S. units, and this agrees with the value usually quoted.\* A piece of the ring was then cut out, so as to provide a straight specimen, having a length about 3.5 cm., and square cross-section (1 cm.  $\times$  1 cm.). This specimen had some of the original surface of the ring left on one side, which was evidently much more magnetic than the remaining three sides. Owing to preliminary tests with a horseshoe magnet, the specimen was magnetised transversely along this particular surface.

It was tested in the balance with the original surface of the ring parallel to the plane of the magnet, and whereas the value of  $\theta$  was 205 with the specimen oriented one way, it was only 30 when it was turned round through  $180^\circ$ . If there were no residual magnetism these values of  $\theta$  should be equal. It was then demagnetised from a maximum force of 2040 C.G.S. units at frequency 54, and the values of  $\theta$  were 154 and 9C and were still very unequal. The original surface of the ring is undoubtedly highly retentive. On grinding off all traces of the original surface the susceptibility of this piece dropped to 0.00048 from the average value 0.001 which it had in the first instance, and from the value 0.0239 in the original ring.

Specimen No. 2 was cut from the same ring and had a circular cross-section of diameter 1 cm. It had patches of the original surface of the ring along its whole length on opposite sides of a diameter. In its first position this diameter was at right angles to the plane of the magnet ring, and the measured susceptibility was 0.00171. On turning the specimen through  $90^\circ$  the susceptibility fell to 0.00145. On turning it further until it was completely reversed (through  $180^\circ$ ) the susceptibility rose to 0.00159. The effect of the patches of the original surface is clearly evident.

Specimens 1 and 2 were then maintained at a temperature of about  $530^\circ$  C. for 100 hours with a consequent increase in the susceptibility on return to atmospheric temperature. The circular bar No. 2 was tested in the first instance just as it left the furnace, and its susceptibility was 0.466, taking an average of two determinations. On polishing the specimen with emery and demagnetising it, the average susceptibility fell to 0.267, which shows directly the effect of a very thin layer of oxide.

Specimen No. 1 had also a high susceptibility, but as it was desired to obtain a susceptibility of lower order, its temperature was raised to about  $750^\circ$  C. and it was allowed to cool in air. It was then polished on emery and demagnetised; the susceptibility was then found to be 0.0957. The specimen was then ground so as to have a circular cross-section, its volume being reduced from 2.36 to 1.729. After demagnetisation the susceptibility was 0.119, which is larger than the value found with the square section, partly no

\* 'Phil. Trans.,' p. 462 (1885); 'The Electrician,' November 9, 1900.



doubt on account of the test being only made with the sides of the square parallel to the faces of the pole-pieces. The instrumental constants given by these two specimens in their final state have the values 132 and  $125 \times 10^{-6}$ .

A third specimen (No. 3), having a circular cross-section, was cut from the original ring, and not so much of it ground away as in the case of specimen No. 1. Its susceptibility had an average value of 0.00453, which is larger than that of the No. 1 specimen before heat treatment, possibly on account of the presence of the original surface of the ring. Its susceptibility was more than twice that of the No. 2 specimen when first tested. Its density was appreciably smaller, probably on account of the existence of small blow-holes, of which there was distinct evidence. It would appear that the susceptibility of this steel as received from the foundry, when all traces of the original surface have been removed, is of the order 0.0004, that is to say, its permeability is of the order 1.005 as against 1.27, the value usually quoted (*loc. cit.*).

(b) *Spiegel Eisen*.—A small piece of this alloy which was supplied to the author by Prof. A. K. Huntington, was ground so as to form a fairly regular test-piece with two of the crystal faces along its length. The piece was 2.6 cm. long, and its cross-section measured 0.48 cm. between the faces, and 0.58 cm. at right angles thereto, the sides being approximately round between the crystal faces. It was highly magnetic and very retentive when received.

It was then heated to bright redness and allowed to cool freely in the air, in order to remove all traces of magnetisation.

Two determinations were made in the balance (a) when the smaller width was parallel to the plane of the magnetic ring, giving  $\theta = 218$ ; and (b) when turned through  $90^\circ$ , the deflection  $\theta$  then being 247. The figures obtained were as follows:—

Volume c.c. V.	Density.	Ampères A.	Magnetising force H.	Deflection $\theta$ .	$\theta/\Delta^3 V$ .
0.44	7.57	0.0213	14.3	218	} $1.16 \times 10^{-6}$
		0.0218	14.3	247	

The value of the susceptibility, as found in the magnetometer with  $H = 53$ , was 0.15 C.G.S. units.

So that the instrumental constant from this investigation was found to be

$$C = 0.15/1.16 \times 10^{-6} = 129 \times 10^{-6}.$$

It is interesting to note that another piece from the same block (not heated) had a susceptibility of 0.487; whereas another specimen (also not

heated) from Prof. Herroun's collection had a susceptibility of 0.114. In both cases heating to redness for a few minutes reduced the susceptibility to about one-third of its original value.

(e) *Slatey Magnetite (Manchuria)*.—A piece obtained by permission from specimen 9500 in the collection of the Geological Survey and Museum, has a volume 0.985 c.c., and density 3.40. When it was tested in the balance the following figures were obtained:—

Direction of magnetic field relative to the laminations.	Ampères A.	Magnetic force H.	Deflection $\theta$ .	$\theta/A^2V$ .
Across laminations .....	0.0092	6.15	92	1,105,000
	0.0125	8.36	150	975,000
	0.0192	12.8	373	1,020,000
With laminations .. . . .	0.0092	6.15	110	1,810,000
	0.0126	8.36	192	1,220,000
	0.0192	12.8	414	1,130,000

The mean value of  $\theta/A^2V$  is 1,100,000, and the susceptibility, as given by the magnetometer with  $H = 53$ , was 0.118. The instrumental constant  $C$  is therefore  $107 \times 10^{-9}$ .

## 12. The Use of Rock Specimens.

(a) *Pisolithic Iron Ore (Dolgelly)*.—This specimen is from the collection of the Geological Survey and Museum, and has a volume of 2.84 c.c. and a density 3.08. Its susceptibility, obtained by the magnetometer, is 0.013. With a current of 0.0136 ampères, corresponding to a magnetic force  $H$  equal to 21.3, the value of  $\theta/A^2V$  is 119,000. The instrumental constant  $C$  becomes in this instance  $0.013/119,000 = 109 \times 10^{-9}$ .

(b) *Magnetite Calcite (Aran)*.—From the Geological Survey and Museum Collection. The volume of this piece was 3.14 c.c. and its density was 3.40. It contained detached magnetite crystals. Its susceptibility, as tested in the magnetometer, had the value 0.141. An additional test was made by inserting the specimen in rectangular holes cut in the pole-pieces of an electromagnet having a core of stalloy. An exploring coil was wound on the specimen and attached to a ballistic galvanometer. Deflections were obtained on reversal of the magnetising current (a) with the specimen in position, and (b) when the specimen was removed, and the exploring coil was supported in its original position on a wooden former having the same size as the test piece itself. The ratio of the deflections indicated a susceptibility of 0.12. When tested in the balance with the current  $A = 0.00935$ , corresponding to a force  $H = 6.25$ , the value of  $\theta/A^2V$  was 1,370,000. The instrumental constant is, therefore, found to be  $0.141/1,370,000$  or  $103 \times 10^{-9}$ .

The work on this particular specimen is of interest in that a new method was adopted. Hitherto the susceptibilities of the materials examined were such that they could readily be tested independently by the direct method of the magnetometer. In connection with the application of such tests, the writer wishes to acknowledge cordially the valuable assistance rendered to him by Prof. E. F. Herroun, F.I.C., who devoted a considerable amount of time to this work and made valuable suggestions with regard to the materials suitable or available for the work. In connection with the present specimen, the susceptibility was of such magnitude that the ring method with the ballistic galvanometer became an experimental possibility, and therefore was adopted as an alternative to the magnetometer.

[*Note added November 13, 1919.*—This method is fully described, and further information on the susceptibilities of the Manchurian and other magnetites is given in a paper read before the Physical Society of London. A portable instrument used in some of this work was shown at the meeting of the Royal Society, at which this paper was read. For details see 'Proc. Phys. Soc.,' vol. 31, Part 5, August 15, 1919.]

(c) *Dolerite from a Coal Shaft, Whitwick, Leicestershire* (L 114).—Report to the Geological Survey and Museum, February 12, 1918. The specimen has an approximately circular cross-section of diameter 1 cm., and its length is about 4 cm. Its volume is 2.90 c.c. and density 2.89. In appearance this rock is much more uniform than, for example, the grey granite (L 15) from Mount Sorrel Quarry, Leicestershire, and its susceptibility is fairly high. It appeared to be suitable for testing the constant of the instrument. There are indications of a cleavage plane parallel to the axis of the cylindrical test piece, and on cutting a portion away a layer of very small crystals of magnetite was discovered. It is apparent, therefore, that the susceptibility obtained is not representative of the whole mass of the specimen.

Demagnetisation was carried out in this case by placing the specimen in a solenoid and varying the force  $H$  from a maximum of 1500 C.G.S. units to zero at a frequency of 50. The susceptibility was slightly increased, showing that there were residual effects in the specimen as received. The average value of  $\theta/A^2V$  is 34,000, and the magnetometer gave a susceptibility equal to 0.0031. The instrumental constant is therefore  $0.0031/34,000 = 91 \times 10^{-8}$  which cannot, however, be regarded as trustworthy.

### 13. *The Use of Powders.*

In a report to the Director of the Geological Survey and Museum, dated December 17, 1917, it was pointed out by the author that if rock specimens

are reduced to powder by a grinder, in the construction of which no magnetic material is used, and then tested for magnetic susceptibility by the instrument now described, the susceptibilities of the original specimens could be obtained. The powders so prepared are placed in a glass tube of known internal volume, the closeness of packing being due to tapping the tube somewhat firmly at intervals during the filling process. Two sizes of tubes have been employed, having internal diameters of 0.867 cm. and 0.535 cm. respectively, and the powder occupied a length of 4 cm. in each case. The superficial or apparent volumes of the contained powders are therefore 2.36 c.c. and 0.900 c.c. respectively. To obtain the volume-susceptibility of the original rock it is necessary to weigh the powder that was in the tube and to find the volume of the solid rock from whence it was obtained—thus making use of the density of the solid specimen.

The permeabilities of powders have in some cases been determined by Crane.\* but his method, which is quite different, appears to be open to serious criticism, and it is not certain that the quantity measured is really the permeability of the specimen. We do not, however, propose to compare the results obtained with those of the present paper, as it would not be readily possible, in view of the totally different origins of most of the materials used.

Accounts are now appended of some of the more typical powders dealt with, and their modes of treatment. They may be regarded as illustrative cases.

(a) *Normal Grey Granite, from Mount Sorrel, Leicestershire (L 15.)*—A piece of this rock (not the specimen tested in the solid state) was reduced to very fine powder by an iron grinder, and gave an extraordinarily high value of the susceptibility which was about 7.5 times the value obtained with a solid piece taken from the same hand specimen. By chemical analysis the powder was found to contain about 0.5 per cent. of metallic iron. Another piece of the same rock was finely ground in a Wedgwood mortar, and this had a susceptibility which was 2.3 times that of the original test piece. Finally, the original test piece was finely ground in a Wedgwood mortar and its susceptibility when referred to the volume of the original rock was very nearly the same as was found with the specimen when solid (see Table I). These results show (a) that in the case of this granite the distribution of magnetite is not uniform, that is to say, pieces of the same rock may have different susceptibilities; (b) if a piece of the granite be first tested in the solid state and then finely ground in a non-magnetic grinder, the susceptibilities are found to agree fairly closely.

\* 'Trans. Amer. Inst. Mining Engineers,' vol. 31, p. 405.

(b) *New Zealand Iron Sand*.—This sand was given to the author some years ago by Mr. C. R. Palairé, and the iron produced therefrom was tested for its magnetic properties.\* The chemical percentage composition of the sand is as follows:—Peroxide of iron 52·88, protoxide of iron 29·60, alumina 0·90, protoxide of manganese 0·48, magnesia 4·0, silica 3·80, titanio acid, 8·41, oxide of cobalt trace, phosphoric acid none, sulphur none: total 100·07.

A mixture of this sand, whose absolute density is 4·70, with hard paraffin whose density is 0·923 containing 25 per cent. by volume of the sand, or 63 per cent. by weight, was used in the production of rods having diameters of 0·72 and 0·92 cm. respectively. The rods were 8 cm. long and, tested in the magnetometer, gave values of the volume-susceptibility 0·0412 and 0·0425 in C.G.S. units. The rods were then cut in half so as to form suitable specimens for the balance and the results obtained were as follows:—

Specimen.	Diameter.	Length.	Volume c.c. V.	Ampères A.	Deflection $\theta$ .	$\theta/A^2V$ .	Susceptibility by magnetometer.	Instrumental constant C.
A	cm. 0·72	cm. 3·9	1·68	0·0173	195	412,000	0·0412	$100 \times 10^{-9}$
B	0·72	4·0	1·59	0·0173	200	412,000		$100 \times 10^{-9}$
A	0·92	4·05	2·69	0·0176	381	455,000	0·0425	$93·5 \times 10^{-9}$
B	0·90	4·09	2·72	0·0176	372	440,000		$96·5 \times 10^{-9}$

When tested alone the volume-susceptibility of this sand is 0·143 taken on superficial or apparent volume:  $\theta/A^2V$  has a mean value of 1,240,000, and the instrumental constant is  $115 \times 10^{-9}$ .

(c) *Northampton Iron Ore* (N 88).—This iron ore is very uniform and has yielded good results. The method adopted was to first test a solid specimen, and then to grind it in a Wedgewood mortar and test it in the powdered state. It will be seen from Table I that in the solid and powdered states the volume-susceptibility is almost exactly the same, namely, 0·00057 C.G.S. units.

#### 14. On the Influence of Size of Tube.

It will be noticed on referring to Table I that the susceptibility in the above cases is slightly larger in the case of the smaller tube. The theory underlying the action of the instrument indicates that this should be the case. This point is tested further, and reference should again be made to the figures given in Table I. The red serpentine from the collection of Prof. E. F. Herroun shows a slightly larger susceptibility when tested in the smaller tube. When referred to the volume of the original rock the

\* 'The Electrician,' September 17, 1897.

Table I.

Description.	Weight.	Volume.		Density of solid.	Magnetising force.		Deflection $\theta$ .	Volume susceptibility in arbitrary units.	
		Superficial V.	Equivalent of solid V.		Ampères A.	C.G.S. H.		$\theta/\Delta^2V$ .	$\theta/\Delta^2V$ .
L 15 Normal granite, grey, Mount Sorel Quarry, Leicestershire, solid	9.008	3.421	—	2.63	0.147	98	415	—	5610
Finely powdered in Wedgewood mortar	3.943	2.36	1.223	2.63	0.0708	47	92	—	5390
	1.212	0.90	0.46	2.63	0.1036	60	199	—	5390
N 66 Partially oxidized collic ore, No. 2 pit, Irthlingborough Tunnel, solid	4.981	1.801	—	2.77	0.1198	80	96	—	5350
Finely powdered in Wedgewood mortar	3.849	2.36	1.380	2.77	0.191	128	258	—	5750
H red serpentine, the Lizard, Cornwall, solid	1.460	0.90	0.526	2.56	0.197	133	102	—	5700
Finely powdered in Wedgewood mortar	5.764	2.36	—	2.56	0.256	171	176	—	5800
H dark green serpentine, the Lizard, Cornwall, solid	3.086	2.36	1.21	—	0.356	200	419	—	2685
Finely powdered in Wedgewood mortar	1.159	0.90	0.452	2.55	0.30	100	104	—	2565
Fe <sub>2</sub> O <sub>3</sub>	5.91	2.318	—	—	0.15	132	177	—	3600
FeO (contains some iron)	3.015	2.36	1.18	—	0.197	172	88	—	2630
Red hematite, circular piece	5.34	1.213	—	4.40	0.257	353	278	—	437
Finely powdered	4.58	2.36	1.037	4.42	0.525	376	234	—	590
Fe <sub>2</sub> O <sub>3</sub>	4.052	2.36	—	—	0.682	457	139	—	660
Fe <sub>2</sub> O <sub>3</sub>	1.455	0.90	—	—	0.142	95	176	—	3730
Fe <sub>2</sub> O <sub>3</sub>	3.323	2.36	—	—	0.142	95	90	—	3770
Fe <sub>2</sub> O <sub>3</sub>	1.205	0.90	—	—	0.268	176	136	—	1610
Fe <sub>2</sub> O <sub>3</sub>	7.40	2.36	1.48	4.98	0.256	172	164	—	2400
Fe <sub>2</sub> O <sub>3</sub>	2.967	0.90	0.59	—	0.358	173	269	—	—
New Zealand iron sand alone	6.720	2.36	1.480	4.70	0.269	174	127	—	—
	2.535	0.90	0.560	—	0.364	244	809	—	—
					0.367	246	154	—	—
					0.020	13.4	247	—	—
					0.0234	16	115	—	—
					0.0162	10.2	683	—	—
					0.0152	10.2	265	—	—
								$2.00 \times 10^5$	$2.08 \times 10^5$
								$1.21 \times 10^5$	$1.27 \times 10^5$

susceptibility of the powdered specimen is slightly larger than when solid. The dark green serpentine, also from the same collection as the red variety, shows a close agreement between the values for the solid and powdered states. A specimen of red hæmatite was finely powdered and its susceptibility when referred to that of the original rock is again slightly larger than in the solid. To contrast with the figures obtained from the red hæmatite,  $\text{Fe}_2\text{O}_3$  has been tested. If referred to a possible solid state the susceptibility of  $\text{Fe}_2\text{O}_3$  powder would be smaller than that of the hæmatite itself. It is noticeable that the smaller tube gives the larger value of the susceptibility. The effect of diameter in the specimen is very marked in the case of  $\text{MnO}_2$  which has also been tested. The only powder so far tested which gives a contradictory result is  $\text{FeS}$ . The solid tested in the magnetometer gave as the susceptibility 0.064. The powder, when referred to the original solid, gives  $\theta/A^2V = 400,000 \times \frac{2.36}{1.48} = 640,000$ . The instrumental constant =  $100 \times 10^{-9}$ .

### 15. *Experiments with Fluids.*

The fluids with which experiments have been conducted are solutions of manganese sulphate and ferrous sulphate in water. These were selected because a certain amount of experimental information has already been obtained, which is of a somewhat contradictory nature, very diverse values for the mass susceptibility having been given by different observers.

The mass-susceptibility ( $K_m$ ) of a solution of such a salt in water is given by the formula

$$K_m = \frac{p}{100} K_{\infty} + \left(1 - \frac{p}{100}\right) K_{m_0}.$$

Where  $K_{m_0}$  is the mass-susceptibility of water, which may be taken as  $-0.75 \times 10^{-6}$ ,  $K_{\infty}$  is the mass-susceptibility of the water-free salt, and  $p$  the percentage weight of salt in the solution. Typical experiments with the solutions led to the following results:—

(a) *Manganese Sulphate*.—The values given in the Landolt-Börnstein 1912 Tables for the mass-susceptibility ( $K_m$ ) of manganese sulphate are

$$(98, 114, 100, 85) 10^{-6} \text{ C.G.S. units}$$

at atmospheric temperatures. The variation among these values is considerable, and serves as a valuable indication of the fact that susceptibilities of this order have not hitherto been determined with precision. The mean of the four values is

$$K_m = 99 \times 10^{-6} \text{ C.G.S. units.}$$

A solution of manganese sulphate containing 0.055 grm. of manganese, or 0.151 grm. of sulphate per cubic centimetre was placed in a test tube having

an internal diameter 0.867 cm., the total volume of the solution being 2.36 c.c.

After correction for the susceptibility of the tube itself, it was found that

$$\theta/A^2V = 190.$$

For this solution,  $p = 15.1$ , and using the mean value of  $K_m$ , we obtain on calculation

$$K_m = +14.5 \text{ C.G.S. units.}$$

The density of this solution is 1.17, so that the volume-susceptibility is

$$K = +16.95 \times 10^{-6}$$

with a corresponding value

$$16.95 \times 10^{-6}/190 = 89.3 \times 10^{-9}$$

for the instrumental constant.

It is clear from the previous determinations that the constant is decidedly larger, suggesting that the value  $85 \times 10^{-9}$  for the magnitude  $K_m$  is greatly in error, and that the mean of the others is more reliable. Adopting these three only, the mean value becomes, from the work of previous investigators,

$$K_m = 104 \times 10^{-6}$$

whence

$$C = 94 \times 10^{-9}$$

which is very close to the value of the constant found from the instrument itself. The third entry in Landolt-Börnstein thus appears the most reliable.

(b) *Ferrous Sulphate*.—Landolt and Börnstein's Tables quote seven values for the mass-susceptibility of this salt:—

$$(93, 75, 82, 84, 75, 37, 51) 10^{-6} \text{ C.G.S. units,}$$

some of which must be very inaccurate. We shall provisionally reject the last two in forming a mean, which becomes

$$K_m = 82 \times 10^{-6}.$$

A solution used had density 1.15 and a value of  $p$  equal to 15.2. We obtain

$$K_m = +11.8 \times 10^{-6}$$

and for the volume-susceptibility,

$$K = +13.59 \times 10^{-6}.$$

The value of  $\theta/A^2V$ , as given by the instrument, and corrected for the glass, was 150. The resulting value of the instrumental constant is  $89.0 \times 10^{-9}$ , but little reliance can be placed on it. The solution contained 0.056 grm. of iron or 0.152 grm. of ferrous sulphate per cubic centimetre, the total volume being 2.36 c.c., as before. The value of  $K_m$  is probably about  $93 \times 10^{-6}$ , the highest previous estimate.



16. *The Final Instrumental Constant and Use of the Balance.*

In the interpretation of the values of the instrumental constant various circumstances must be borne in mind. For example, that given for manganese alloy of susceptibility 0.33 can be of little value. For the method is not really applicable to such large susceptibilities without considerably more mathematical development of the higher approximations. The criteria, which, in fact, define the applicability of any direct method of measuring  $K$ , are set out in Maxwell's treatise,\* and are well known. When the susceptibility exceeds a certain small amount—determined greatly by the diameter of the specimen—the demagnetising forces must be accounted, and the simple expression  $\frac{1}{2}Kd(H^2)/dx$  for the mechanical force per unit volume cannot be used. It was nevertheless of interest to include this value, as showing the extent of error involved.

The values for many rock specimens, moreover, are unreliable, on account of the difficulty of securing an even approximately homogeneous specimen, especially as regards its magnetic content. This source of error applies, to a greater or less extent, to all the specimens, but is likely to act in a fortuitous direction among the species.

The results with solutions have already been discussed sufficiently. The general mean of the results is taken without the use of Spiegel Eisen and manganese alloy. It is not, however, altered appreciably if they are included. The average relates to rock specimens and minerals generally.

The general mean, taken as above, is  $C = 104$ , and no appreciable divergence occurs if the values are weighted according to any probable system. The constant deduced from the instrument itself was  $C = 93.6$ , and the general agreement may be regarded as satisfactory.

17. *The Effect of Length and Shape of Cross-section of the Specimen.*

The variations in the form of cross-section and length of the specimens were investigated somewhat fully. The results demonstrated that the dimensions selected were satisfactory, and it is not thought necessary to give an account of this part of the work.

18. *Magnetic Susceptibility of Varieties of Mica.*

A representative series of micas was tested by the author some years ago for dielectric strength, capacity, and insulation resistance,† and, as specimens of these were available, they have now been tested for susceptibility by the balance.

\* 'Elec. and Mag.' vol. 2, p. 67, Edition 1873.

† 'The Electrician,' December 18, 1904, and March 17, 1905.

Table II.—Mica.

No. of Specimen.	Description.	Weight in air.	Volume, c.c. V.	Density.	Amperes $\Lambda$ .	Magnetising force H.	Deflection $\theta$ .	Volume susceptibility.	Ratio.
1	Madras, brown, heavily spotted	7.035	2.70	2.83	0.0837	22.5	317	$\frac{\theta}{\Lambda V}$ . 103,000	22.8
1A	" " very slightly spotted	7.215	2.64	2.73	0.1025	69	98	11,300	
2	" " green, spotted	7.007	2.70	2.83	0.247	163	232	4,500	3.96
3	" " "	7.495	2.65	2.83	0.266	103	56	1,370	
4	" " "	6.945	2.50	2.78	0.233	173	103	346	3.89
5	" " stained	6.440	2.325	2.77	0.247	173	64	1,410	
6	" " ruby, much stained	7.072	2.87	2.75	0.0777	51.6	230	363	11.3
7	" " clear green	7.273	2.55	2.84	0.233	156	187	1,610	
8	" " "	7.367	2.59	2.84	0.0865	53	174	1,290	8.57
9	" " clear pale green	8.150	2.87	2.84	0.247	233	326	1,080	
10	Bengal, ruby, spotted	7.108	2.54	2.80	0.5125	345	161	1,199	1.25
11	" " much stained	8.083	2.56	2.73	0.5125	345	129	23.3	1.24
12	" " white	7.812	2.80	2.79	0.563	391	93	106	
13	Bengal yellow	8.235	2.99	2.76	0.583	391	75	85.5	
14	" " ruby, clear	6.333	2.235	2.835	0.583	391	272	312	1.15
15A	Canadian, silver amber	6.562	2.375	2.56	0.583	391	239	272	1.32
15B	" " amber	6.460	2.295	2.81	0.583	391	270	280	1.10
15C	" " "	7.532	2.06	2.83	0.583	391	253	266	
16	South American, spotted	7.310	2.595	2.82	0.583	391	220	134,000	51.3
17	" " ruby, clear	7.432	2.03	2.84	0.583	391	220	2,610	1.21
					0.1786	20.7	332	93.5	8.5
					1.01	672	333	77.2	1.24
					1.01	672	401	132	1.27
					0.969	670	236	106	1.36
					0.9425	630	239	86	
					0.872	535	178	68.4	
					0.867	530	180	107	
					0.877	537	137	79	
					0.872	533	137	119	
					0.867	530	173	99	
					0.96	640	246	116	
					0.963	647	180	84	
					0.856	573	297	153	
					0.850	570	212	110	
					0.0003	40	398	42,500	
					0.251	168	233	1,680	25.7
					1.03	670	464	154	1.17
					1.03	670	361	131	

N.B.—In the case of each specimen the susceptibility first given was taken in the direction of the laminations.

Each specimen was built up of laminæ about 3.85 cm. long, and of varying width, so as to produce an approximately circular cross-section 1 cm. in diameter. There were from 12 to 16 plates in each specimen, which were held together by two turns of fine cotton round each end. Each specimen has been tested with the direction of the magnetic field parallel to the planes of the laminæ and at right angles thereto. On reference to Table II, it will be noticed that, in each specimen, the susceptibility is larger in the former case. The ratio of the susceptibilities parallel to and at right angles to the plane of the plates is much more pronounced in the case of the spotted micas. For example, Nos. 1 and 10 give the remarkable ratios 22.9 and 51.3. Spotted specimens contain oxide of iron as inclusions, and under the microscope distinct crystals of magnetite in laminæ are visible, hence their high susceptibility. Clear ruby mica (Nos. 14 and 17) is almost exclusively used for high grade condensers, and its susceptibility, though small, is not the smallest of the series. The ruby (Nos. 6 and 11), much stained by kaolin inclusion, has very low susceptibility, as also has the yellow variety (No. 13). The amber series (Nos. 15 A, 15 B, 15 C) have also a low susceptibility.

The results obtained in different directions would appear to imply an orderly arrangement of the included particles of oxide of iron, or an actual difference in behaviour of the mica itself in different directions with relation to the crystal axes. The attempt has not been made in the present communication to decide between these alternatives, but the phenomenon is so marked that it appeared desirable to place it on record.

### 19. *Susceptibility of Aluminium.*

The physical properties of certain alloys of aluminium were examined in 1901,\* and since that time the specimens have been on the roof of King's College, London, in order to investigate the effects of exposure. Pieces of the original wires have been preserved, and a selection from these has been made for the purpose of investigations on susceptibility. Each specimen, with the exception of No. 26, has a length of 4 cm. and a diameter of 0.32 cm. Referring to Table III, No. 25 is a piece of commercial aluminium, whose conductivity is 61.5 per cent. of that of pure copper. Using the constant  $111 \times 10^{-9}$  the volume susceptibility is  $+4.95 \times 10^{-6}$  C.G.S. units. The volume susceptibility of pure aluminium is stated to be  $+1.8 \times 10^{-6}$ ,† and its mass susceptibility  $+0.65 \times 10^{-6}$ .‡ No. 21 was chosen on account of

\* 'Journal of Proceedings of the Institution of Electrical Engineers,' Part 154, vol. 31 (1903).

† Landolt-Börnstein 1912 Tables.

‡ Kaye and Laby Tables.

its comparatively large iron content. Comparison with No. 23 would indicate that manganese has the effect of increasing susceptibility. It has been shown earlier that a normal solution of  $\text{MnSO}_4$  has a higher susceptibility than a similar solution of  $\text{FeSO}_4$ . Again, it is well known that copper-manganese alloys of aluminium can have high susceptibility. No. 22 has about the same percentage of nickel as No. 21, but its iron content is much smaller. This alloy (No. 22) is remarkable on account of its high breaking load, which is 45,900 lbs. per square inch of cross-section, as against 28,200 for commercial aluminium (No. 25). There is also a great difference between the temperature coefficients of electrical resistance of these alloys. That of No. 22 has the value 0.00178 as against 0.00393 for No. 25. No. 20 has also a high breaking load (38,600 lbs. per square inch) as compared with No. 25, and its susceptibility is slightly higher. The chief characteristic of specimen No. 26, whose length is 4 cm., is the presence of 1.97 per cent. of cobalt. Its susceptibility is not much higher than that of pure aluminium. The low value found in this specimen may be influenced by its relatively large diameter.

Table III.—Alloys of Aluminium.

No.	Chemical analysis.						Weight of specimen.	Density.	Magnetising force H.	Volume susceptibility, $10^{-6}$ C.G.S. units.
	Si.	Fe.	Cu.	Ni.	Mn.	Co.				
							gm.			
25	0.14	0.31	—	—	—	—	0.892	2.715	600	4.95
21	0.39	2.57	0.10	1.39	—	—	0.845	2.770	600	9.37
23	0.44	0.56	0.09	—	1.78	—	0.865	2.750	605	9.80
22	0.37	0.43	1.08	1.29	—	—	0.892	2.747	592	6.48
20	0.37	1.10	0.06	2.25	—	—	0.853	2.756	582	5.37
26	0.33	0.56	—	—	—	1.97	8.70	2.77	585	2.76

*20. Note on the Susceptibilities of Glasses in Relation to Composition.*

In some recent confidential work on the electrical conductivity of a series of glasses as affected by temperature, the author had an opportunity of using the balance as a detector of the amounts of oxides present in their composition. The hard glasses having high electrical resistance are characterised by their negative susceptibility which may be as high as  $-15 \times 10^{-8}$  C.G.S. units. On the other hand, the low resistance glasses may have positive susceptibility as high as  $+233 \times 10^{-8}$  C.G.S. units.

Determination of magnetic susceptibility promises to be of some value in the investigation of glasses, and possibly of some of the raw materials used in glass manufacture. There is evidence that the method would give rapidly

the relative amounts of ferrous iron present in samples of glass, and results obtained with glasses containing known amounts of ferrous iron could be tabulated so as to obtain the actual amount of ferrous iron in any glass. It is, of course, possible with further experiments that magnetic susceptibility may be found in glasses free from iron. The influence of manganese and many other constituents has yet to be investigated.

### 21. *Note on the Susceptibility of Tourmaline.*

It is well known that the magnetic susceptibility of certain crystals is a variable depending upon the direction in which it is measured. Weiss\* has examined crystals of magnetite and has determined the absolute values of the susceptibility in terms of direction and intensity of magnetising force. He has shown that the susceptibility for moderate values of the force differs according to direction, and that the ultimate susceptibility in any direction tends to the same value when the force is sufficiently large. The author has had an opportunity of examining the magnetic properties of four specimens of tourmaline. A good specimen of green tourmaline was lent by Dr. T. R. Merton. It is in the form of a rectangular plate 0.291 cm. thick and measures 1.360 cm. in the direction of its principal crystallographic axis, and 1.305 cm. at right angles thereto. When tested in the balance in these two directions it was found that the susceptibility at right angles to the principal axis was greater than in the direction of the principal axis in the ratio  $630/543 = 1.16$ . The dimensions of this specimen precluded an accurate statement as to the absolute value of the susceptibility. Dr. W. T. Gordon has prepared from his collection three specimens each in the form of a cube. Two of these were cut from a large crystal, and described as being dark blue opaque. When tested in the balance both these specimens showed the same effect, namely, that the susceptibility in the direction of the principal axis is smaller than in the other two directions at right angles to it. The ratio of the susceptibility at right angles to the principal axis to the susceptibility in the direction of this axis is  $103/86 = 1.20$  and  $130/111 = 1.17$  in the two cases. The larger values of the susceptibility in the case of the smaller cube is partly attributable to its higher density, and partly to its smaller dimensions. The third specimen was cut from a rose coloured crystal (rubellite), and was too feebly magnetic to be accurately measured in the balance with the strong suspension. A number of complete crystals were roughly tested, some of which were a light green colour at one end and rose colour at the other. It was evident that in all cases the green

\* 'Jour. de Phys.,' 3rd Series, vol. 5, p. 435 (1896).

coloured end was the more magnetic. The results of the experiments are embodied in the following Table:—

Specimen.	Volume c.c. V.	Density.	Dimension in direction of mag- netic field.	Ampères A.	Deflection θ.	$\theta/\Delta^2V$ .	Volume susceptibility in $10^{-6}$ C.G.S. units.
Tourmaline plate, green	0.48	3.10	cm. 1.38*	0.785	161	543	—
			1.305	0.789	189	680	—
			0.291				
Tourmaline cubes, dark blue opaque	1.048	3.186	1.01*	0.475	165	761	+ 85.9
			1.028		223	942	+ 108.6
			1.01		221	933	+ 102.6
	0.2755	3.206	0.965*	0.500	223	1014	+ 111.5
			0.959		264	1208	+ 132.6
			0.958		256	1170	+ 128.7
Tourmaline cube, rose	0.96	3.08	0.99	1.05	3	2.83	+ 0.31

\* Principal crystallographic axis.

## 22. General Note on the Susceptibility of Rock Specimens in Relation to the Field of the Earth.

A series of reports on a detailed survey of the susceptibilities of rock specimens dated November 12, 1917, December 17, 1917, January 18, 1918, and February 12 and 27, 1918, was made by the author to Sir A. Strahan, F.R.S., Director of the Geological Survey and Museum. They may be referred to for more detailed results obtained with the present instrument, and the work therein described has the advantage that the specimens mainly come from one particular district (Melton) in which magnetic observations have been made by Dr. G. W. Walker, F.R.S.

A re-testing of some of the specimens therein dealt with has since been performed, and as in some cases the re-testing has been performed "after demagnetisation," some explanation of this process and some remarks which it calls for are desirable. It is well known that if a piece of iron be subjected to a considerable magnetising force, and then tested for permeability at lower forces, the permeability then found is smaller than would have been found had the specimen been first demagnetised. The complete previous magnetic history of rocks is unknown, but some of them owing to their retentivity show that they must have acquired a high degree of magnetisation at some time. By subjecting such a specimen to an alternating magnetic force of gradually diminishing magnitude until it ultimately vanishes, the magnetic effects due to this retentivity which have perhaps existed for

## 454 *The Measurement of Magnetic Susceptibilities of Low Order.*

centuries can be removed in a few minutes, and it is then found that the specimen (for example, the dolerite E 6519) may have an increased susceptibility. In connection with magnetic survey work generally, this retentivity and previous magnetic history appear to play an important part, because the existing magnetic effects of certain rocks are not obviously connected with the existing magnetic field of the earth. The low grade ores (for example, N 88) are typical of those rocks which have a small or negligible retentivity, but certain types of rocks in which magnetite occurs have pronounced retentivity. It would seem, therefore, that the magnetic effects exhibited by these low grade ores may be due to the existing earth's field, or to the joint action of this field and the retained magnetism of the more basic rocks. The subject is one of great complexity, and it does not appear to be satisfactory in all cases to attribute magnetic observations solely to the effects of the existing general field of the earth.

### 23. *Summary.*

(1) The present paper contains an account of an instrument which has been designed for the measurement of magnetic susceptibility of low order, together with some of the results to which it has led. It depends for its action upon the pull exerted by an electromagnet in accordance with the well-known Maxwell expression for the mechanical force exerted upon unit volume of the substance. This mechanical force is balanced against the force of torsion in a phosphor-bronze strip.

(2) A considerable portion of the paper is devoted to the determination of the instrumental constant, from data obtained directly with the instrument itself, and by the employment of substances whose susceptibilities had been measured by other methods. In this connection a modified method of using a ballistic galvanometer has been devised which leads to greater sensitiveness. In addition to rock specimens, other substances have been used, and in their employment some interesting results have been obtained. For example, it is shown that the susceptibility of 13 per cent. manganese alloy is much smaller than is usually supposed.

(3) The susceptibility of powdered rock specimens has been measured and compared with that of the solid. A very fair agreement has been obtained between the two, and the method has the advantage that powders can be rapidly made. Care has, however, to be taken in their preparation.

(4) The susceptibilities of varieties of mica have been measured, and it is shown that in certain cases in any direction parallel with the laminae the susceptibility may be over fiftyfold that obtained in a direction at right angles thereto.

(5) A series of light aluminium alloys has been tested with the balance, and it has been found that, whereas the susceptibility of commercial aluminium is increased by alloying with copper and manganese, it is diminished by alloying with cobalt.

(6) In a note on the susceptibility of glass in relation to composition it is shown that the balance could be used to rapidly determine the relative amounts of ferrous iron in different specimens of glass.

(7) Certain specimens of tourmaline have been examined. The green and dark blue opaque varieties have susceptibilities in the direction of the principal crystallographic axis varying from 16 to 20 per cent. less than in a direction at right angles thereto. The susceptibility of rose-coloured tourmaline is very small in comparison.

(8) The paper concludes with a note on the retentivity of rock specimens and its possible influence upon magnetic disturbances in magnetic survey work.

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*On the Variations of Wave-length of the Oscillations generated by Three-electrode Thermionic Tubes due to Changes in Filament Current, Plate Voltage, Grid Voltage, or Coupling.*

By W. H. ECCLES, D.Sc., and J. H. VINCENT, M.A., D.Sc.

(Communicated by Prof. W. H. Bragg, C.B.E., F.R.S. Received November 20, 1919.)

It is well known that a circuit containing a condenser and inductance coil can be maintained in oscillation at a frequency near its natural frequency by aid of a three-electrode thermionic vacuum-tube and suitably connected batteries. It is also known that although the frequency of the oscillations depends mainly upon the magnitudes of the inductance and the electrical capacity it is also affected by the resistance in the oscillatory circuit, by the voltages of the various batteries in use, by the temperature of the filament supplying the electrons, by other properties of the vacuum tube, and by the coupling between portions of the circuit associated with the grid and the anode.\*

It is again well known that when one such vibrating circuit is caused to induce current in an independent oscillating circuit the induced current beats

\* See, for example, a paper by W. H. Eccles, "Vector Diagrams of some Oscillatory Circuits used with Thermionic Tubes," 'Proceedings of the Physical Society of London,' vol. 31, Part 3, April 16, 1919.



with the local oscillatory current, the beat frequency being equal to the difference between the frequencies of the induced and the local oscillations. This is applied, for instance, in the so-called auto-heterodyne or endodyne method of reception familiar in wireless telegraphy, where the difference of the high frequencies is arranged to be of acoustic frequency so as to operate the telephone receiver connected with the local oscillatory circuit. In this application the operator varies the pitch of the sound made by the beats by altering the capacity of his tuning condenser. Starting with the variable condenser adjusted to an extreme position such that the local frequency is, say, 10,000 per second lower than the frequency induced by the distant apparatus, a very shrill note is heard in the telephone, and as the local condenser is diminished in capacity, the pitch falls continuously through all the audible octaves till the beats are so slow, say 30 per second, that they cease to form a note.

Continued reduction of the capacity brings a condition in which the beats are below the lower limit of audition till at last the local circuit is "in tune with" the distant oscillator and there are no beats. Further reduction of the local capacity brings the local frequency higher than that of the distant apparatus, and when this difference reaches about 30 per second the beats become audible again; continued gradual reduction of the capacity now causes the pitch of the note to ascend the scale, till at length it disappears beyond the upper limit of audition.

In the following pages, when "the region of silence" is spoken of, the adjustments of the apparatus implied are those in which the relative frequency of the two co-operating maintained oscillations is less than about 30 vibrations per second. The "region of silence" is not actually utilised in the experiments; we found the most advantageous method in our work of tracing the small changes of frequency brought about in either circuit, was to adjust the apparatus so as to obtain a note of convenient pitch and to observe changes in this pitch.

The object of the present investigation was to study experimentally the effects of altering each of the chief variables, with a view to finding the conditions most favourable for the production of continuous waves of constant frequency.

#### *Apparatus.*

- Two oscillating circuits were set up on two work benches placed a few feet apart, and were maintained in oscillation separately by small thermionic tubes of the kind used in the British Army. In addition to the maintained oscillatory circuits, a third circuit was set up on Bench 1. In this a crystal detector and direct-current micro-voltmeter were connected. This third

circuit will be called the crystal circuit. When not being used its inductive coil was removed.

Bench 2 circuit differs from that on Bench 1, in that the plate battery which connects with the oscillator is broken to insert a telephone. The plate battery and telephone are shunted by a condenser (C.T., fig. 1). The circuits on Benches 1 and 2 cooperate to affect the telephone, because of the presence of the linking coils shown at the top of fig. 1.

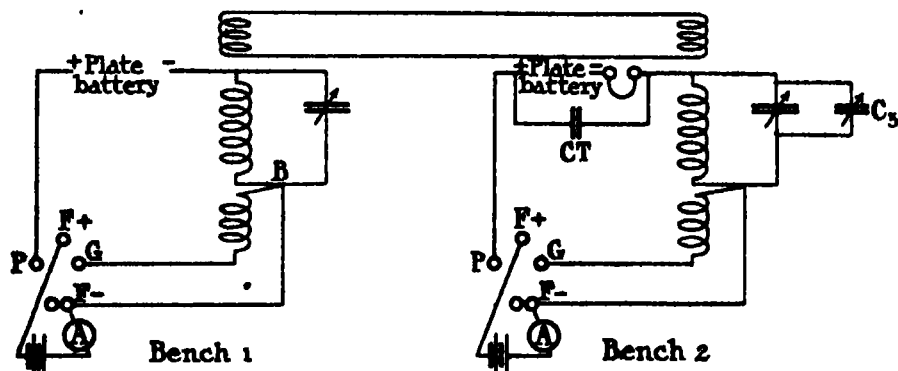


FIG. 1.

The electrical capacity in Bench 2 circuit is made up of two condensers, one of relatively large and fixed capacity, and the other,  $C_3$ , of smaller capacity joined in parallel with the first. The small condenser could in some experiments be used for adjusting the frequency of Bench 2 circuit throughout a series of changes in the Bench 1 circuit, so as to keep the circuits at a fixed difference of frequency. In other cases, however, when the changes in frequency in the Bench 1 circuit were large, the larger condenser was used. Both condensers were calibrated.

#### *Method of Observation.*

The tuning was done by beats. The capacity of the condenser in the Bench 2 oscillator was first adjusted until a musical note was heard in the telephone. There are two possible adjustments for this, one on either side of the position of silence. If necessary, the capacity in Bench 2 was changed so that the setting of the condenser was on that side of the position of silence in which increasing the capacity raises the pitch of the note. The note was next tuned to unison with a tuning-fork heard simultaneously. This fork has a frequency of 256 complete vibrations a second. There are now two closely adjacent values of the capacity in which one beat per second is heard. That setting of the condenser in which the capacity is the larger of

these two values gives a frequency to the Bench 2 circuit, which is less than that of the Bench 1 circuit by 257 complete vibrations a second. The accurate adjustment of the beat to one per second was accomplished by aid of a metronome.

*Effect of Change in Filament Current on Wave-length.*

The wave-length of an oscillator is altered slightly by changing the filament current. As the filament current is raised from the lowest value for which a note is heard in the telephone, the wave-length rises to a maximum, and for further increase in the filament current the wave-length decreases. This is shown in fig. 2, which gives the results of one of many sets of observations all agreeing in their general character. The actual position of the curve on the axis of filament current, and its shape, will depend on the tube itself as well as upon the circuit in which it operates. For these measurements the Bench 2 filament current was kept constant, while that in the Bench 1 tube was altered. The wave-length in this particular apparatus reaches a maximum when the filament current is about 0.77 ampère. The actual values of the changes in wave-length can be readily computed from the known constants of the Bench 2 circuit. In this case the total change of wave-length from the lowest value to the maximum is about 0.3 per cent., that is about 9 metres, since the waves were 3000 metres long.

If now the filament current in the tube of Bench 1 oscillator be kept constant, and that in the Bench 2 oscillator varied, then the compensatory changes in the Bench 2 condenser will be of opposite sign. The tendency towards increase in wave-length due to increase in the filament current has to be compensated by a decrease in capacity to keep the wave-length unaltered. We should thus expect the condenser settings and filament current curve to be somewhat of the same shape as that of fig. 2, but upside down. This was, in fact, the case, as is shown in fig. 3.

The generation of oscillations of maximum wave-length by a maintained circuit of the type shown in fig. 1 is not dependent on the exposure of the tube to the air of the laboratory. Similar curves are obtained whether the valves are covered by a bell-jar or not. Nor does this effect depend for its occurrence on the plate voltage having any particular value. One may alter the plate volts from 70 to 125 without materially changing the shape of the curve, and, when this is done, the maxima occur at values of filament current which are not far apart. It is to be noted that the actual values of the condenser settings at the maxima are not the same with different plate voltages. This is discussed below. The curves shown in fig. 4, in which the plate voltages are varied, are thus to be regarded as set down arbitrarily in

respect to the condenser readings, the datum line varying from curve to curve.

Thus the wave-length emitted by an oscillation apparatus is a function of

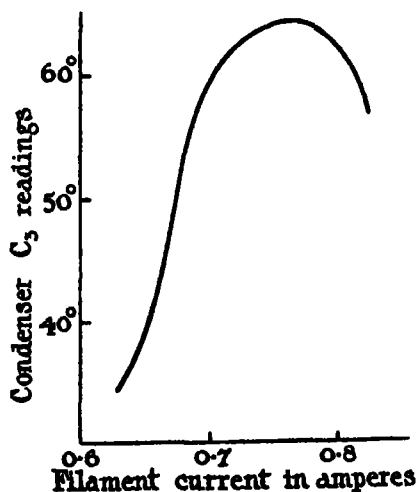


FIG. 2.

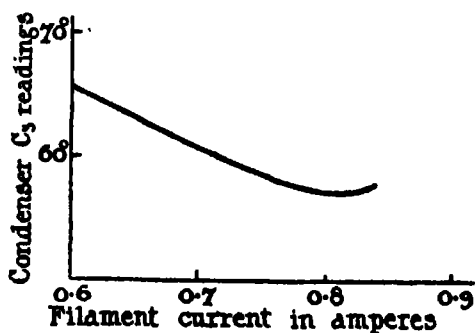


FIG. 3.

the filament current; it is a maximum for a definite current which is not greatly changed by altering the plate voltage. This has been found to occur

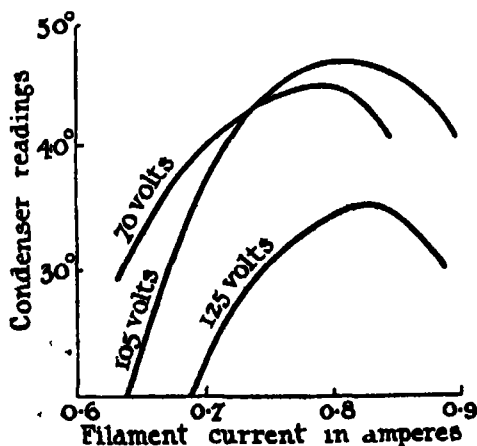


FIG. 4.

in different circuits with different values of inductance and capacity. In this description of the effect of filament current on wave-length, it has been assumed that the coupling between the grid coil and oscillator coil was neither closer than is necessary to maintain the oscillations while the

filament current varied from 0.65 to 0.85 ampère, nor so loose as to make the oscillations too feeble for telephone tuning by beats. If these restrictions are removed, the above statements are still true, but the whole of the curves of the type of fig. 2 may not be accessible for experiment. This will be dealt with further in the last section.

The method of utilising the existence of this phenomenon to obtain constancy of wave-length, in laboratory work of the kind to be described later in this paper, is now clear. In such cases two oscillatory circuits are set up, and one (say the Bench 2 circuit) is used as a delicate wave-meter to study small differences in the wave-length of the oscillations of the other. The Bench 1 circuit has its constants fixed, including a temporarily stationary value for its filament current. The Bench 2 circuit is now used to draw a curve for its own tube like fig. 3. This fixes the filament current to be used in the Bench 2 circuit. In this connection it may be worth noting that, when this current has been determined, no change should be made afterwards in the Bench 2 circuit except the small adjustments of its condenser necessary for tuning. The tube maintaining the oscillations in the Bench 1 circuit is now studied, and a curve like fig. 2 drawn.

We have now determined both filament currents so as to give a constant wave-length in their respective circuits in spite of the unavoidable small variations of filament current. When this is done, the beats heard due to the interference of the notes of the telephone and tuning-fork are, under good conditions, very distinct and steady. That is to say, the frequencies of the two sets do not separate as much as 1 part in 100,000 during the lapse of several minutes. Difficulty is sometimes experienced in getting satisfactory settings of the Bench 2 condenser, but this is usually due to the fact that the telephone note is not pure. And, again, a series of readings may be spoilt by the observer unwittingly setting the condenser so as to allow a note present in the sound from the telephone, but not the fundamental, to masquerade as the fundamental. This is apt to occur in cases when the fundamental is weak or when the fundamental due to any cause has fallen into the region of silence. When the filament currents are adjusted as above the beats are easy to hear, and steady enough for the observer to feel confident of the condenser readings. If the fundamental is inaudible, the beats which can still be heard are spurious, and can be distinguished by their unsteadiness and faintness.

It may happen that on drawing the curve for the change in wave-length with filament current the maximum is not in the range of permissible filament current. It has been found that this is due to the coupling between

the grid coil and main oscillator coil being unnecessarily close. On separating the coils the curve can be made to assume its typical form (fig. 2). If the separation is pushed too far, however, the oscillations may be too feeble before the maximum wave-length is attained.

#### APPLICATIONS OF THE ADJUSTMENTS DESCRIBED ABOVE.

##### *Effect of Change of Plate Voltage on Wave-length.*

This was investigated with the apparatus already described. The increase in capacity in the Bench 2 circuit necessary to keep it in tune, as the plate voltage was increased in the Bench 1 circuit, is shown in fig. 5, which gives the combined results of two sets of observations as a smoothed curve. Other observations gave the curve more nearly as a straight line, but this subject was not studied sufficiently for us to be sure of the exact shape of the curve.

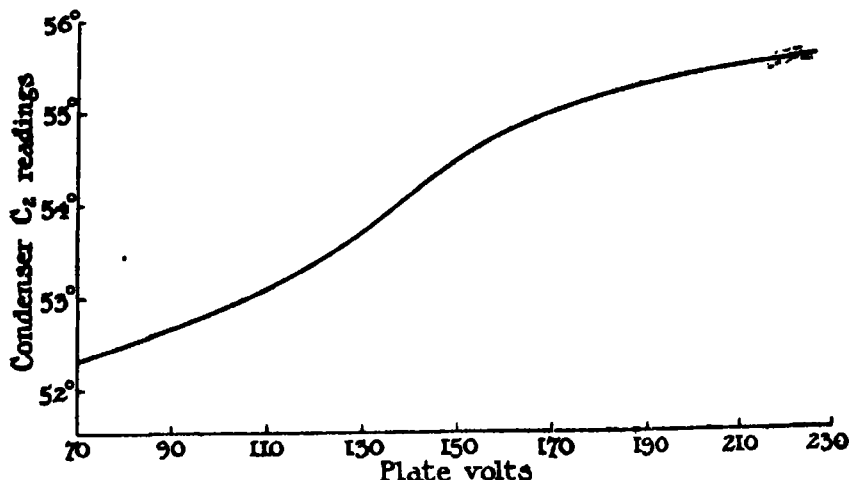


FIG. 5.

The wave-length always increases with increase of plate voltage and a determination of the approximate magnitude of the effect was made. When the wave-length was about 3000 metres and the plate voltage of the tube in the Bench 1 circuit was 130, raising the voltage by 10 increases the wave-length by 6 metres, approximately.

It is worth while considering if this effect is capable of explaining any appreciable part of the change in wave-length with variation of filament current. The mean difference of potential between the plate and the filament (see fig. 1) depends to a small extent on the current in the filament. When this is zero the difference of potential is equal to the plate voltage; but when a current is flowing in the filament in the direction indicated in fig. 1, the

mean potential of the filament is raised, and thus the effective mean plate voltage is decreased by approximately half the fall of potential along the filament. So that when the filament current increases, this effect on the plate voltage decreases the wave-length emitted. But for this curves like fig. 2 would be steeper on the ascending side than they are.

In order to test this point a set of readings of current and voltage on the filament terminals was taken, and the lowest curve on fig. 4 redrawn, with and without allowing for the influence of current on plate voltage. The result is that the effect is not of sufficient magnitude to make any noteworthy alteration in the curves. If the points for 0.65 ampères are taken as coincident, the correction at the maximum only amounts to one-tenth of 1 degree of the condenser in fig. 4.

The immediately applicable lesson taught by these experiments on plate voltage is that plate batteries cannot with impunity be changed or charged during a set of experiments. If a long investigation is in progress care must be taken to keep the plate battery up to a definite voltage, but for work lasting a few hours the small changes in the electromotive force of a good plate battery due to its discharging will not be likely to give any marked change in wave-length.

#### *Effect of Change in Grid Voltage on Wave-Length.*

The battery of cells was introduced between B and the grid coil in the Bench 1 circuit (fig. 1) without any kind of potential divider or other mechanical device for altering the applied electromotive force. This alteration was brought about by connecting the cells up in different ways by wires. This crude method of varying the electromotive force was used because of trouble experienced in preliminary experiments, due to changes in inductance and capacity produced by using potential dividers and commutators. Six small (30 ampère-hour) accumulators were placed in a crate and care was taken that all the cells were in metallic connection for each voltage. In this way the results shown in fig. 6 were obtained. The point on the curve for -4 volts is marked with a note of interrogation as the Bench 2 condenser could not be set to produce audible beats between the fundamental and the fork. When the grid voltage was given numerically greater negative values the oscillations ceased.

It is seen from fig. 6 that from -2 to 4 volts the curve is nearly straight, but for higher values of the electromotive force it bends over slightly towards the axis of volts. For this tube and circuit (250 cm. capacity, 8 millihenries) the increase in wave-length is about 10 metres per volt rise in grid voltage, the wave-length being 2750 metres approximately.

One is warned by these results on grid voltage to beware of the change in wave-length produced by inserting electromotive force in the grid circuit. It

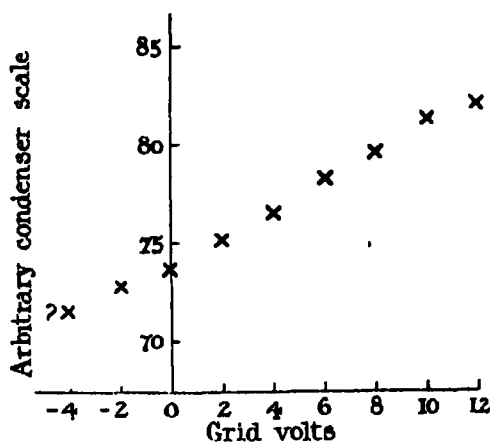


FIG. 6.

is of equal importance to be on one's guard against the effects produced by any change in capacity or inductance that may accompany the alteration in electromotive force.

*Effect of Change in Coupling of Grid Coil and Main Oscillator Coil on Wave-length.*

In the first section of this paper it has been necessary to refer to the effect of closeness of coupling upon the curve giving the wave-length as a function of the filament current. Some experiments were performed which show that the coupling has a marked effect on the wave-length, other things being fixed.

For a given filament current the closer the coupling the greater the wave-length. For different filament currents the wave-length and filament current curve becomes steeper and its maximum moves towards higher currents as the coupling gets closer. These results are shown graphically in fig. 7.

The five points on the capacity scale for 0.7 ampère filament current are for five different amounts of coupling. Each point represents the added capacity on the Bench 2 circuit necessary for tuning. The grid coil was removed 1 cm. further into the main coil between each pair of points as we pass upwards on the capacity scale. The five curves show the effects on the shape of the curve of the type of fig. 2. We get the typical curve with its maximum in curve *d*. If the coupling is much less the oscillations are too weak for the whole range to be drawn, as in *e*. If the coupling is made closer the curve



gets steeper, the wave-length increases, and the maximum moves to a higher filament current (curve *c*).

In curve *b* the grid coil has been pushed too far into the main oscillator

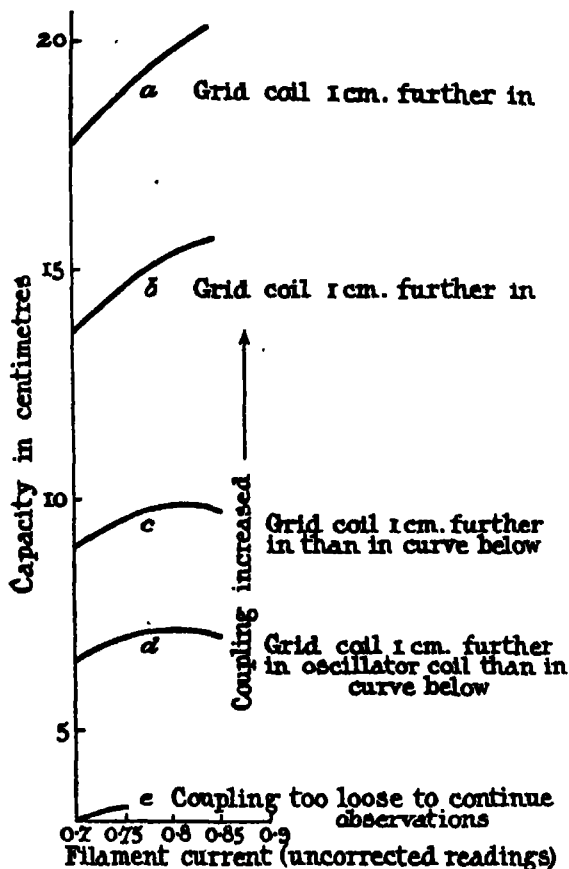


FIG. 7.

coil. We cannot get the maximum without overheating the filament; it has passed out of the diagram to the right. In curve *a* the coupling is so close as to have increased the wave-length materially, and the rising slope of the curve is nearly a straight line. Another set of observations with still closer coupling gave the rising portion of the curve as almost a straight line and still higher up on the diagram.

The variation of coupling gives us a means of putting the wave-length and filament current curve into a position on the axis of filament current in which its maximum is available for use. The coupling can besides be increased so as to give us a filament current and wave-length curve in which

a small change in current produces a large change of the same sign in the wave-length. This property could be applied, for example, to give modulation of wave-length, such as is sought in wireless telephony, or to form the basis of a new method of amplification. In this case the electrical stimulus to be amplified would be introduced into the filament circuit by means of a transformer. The consequent change in wave-length would be the index showing the receipt of the stimulus.

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*Equal Parallel Cylindrical Conductors in Electrical Problems.*

By F. J. W. WHIPPLE, M.A.

(Communicated by Dr. C. Chree, F.R.S. Received June 16, 1919.)

In a recent paper\* Dr. Alexander Russell has called attention to the practical importance of the electrostatic problem of determining the distribution of charge and of potential when parallel cylindrical conductors are electrified. Russell points out that the same analysis will serve for the calculation of the current density and the magnetic flux when currents of high frequency pass along the parallel conductors. The solution he gives for the case of equal and opposite charges (or currents) in the two conductors is exact, but in the general case a more elaborate investigation is necessary.

In the present paper the problem is solved by the method of conjugate functions. For the most part, the results are given in forms convenient for numerical calculation. The investigation is confined to the case in which the two cylinders are of the same size; for this case ordinary Jacobian elliptic functions suffice though in general theta-functions are required and the algebra is rather heavy. It is hardly to be supposed that a problem of such a simple character in a favourite field of investigation has not been solved before. It is desirable, however, to have the solution in an accessible form.

2. *Notation.*—The problem to be considered is virtually in two dimensions, the cylinders being represented by circular sections.

Let  $a$  be the radius of either circle,  $2c$  the distance between the centres,  $2f$  the distance between the limiting points  $\Omega$  and  $\Omega'$ .

Take the origin midway between the centres and the axis of  $X$  along the

\* "Electrical Theorems in connection with Parallel Cylindrical Conductors," 'Phys. Soc. Proc.' vol. 31, p. 111 (1919).

line joining them. The position of a point P may be defined by curvilinear co-ordinates  $u$  and  $v$  such that the angle  $\Omega P \Omega' = u$ , and  $\Omega' P / \Omega P = e^v$ , which relations are equivalent to the equation

$$x + iy = ef \cot(u + iv)/2, \quad (1)$$

or to

$$x = f \frac{\sinh v}{\cosh v - \cos u} \quad (2)$$

with

$$y = f \frac{\sin u}{\cosh v - \cos u}. \quad (3)$$

The two conducting circles are given by

$$v = \pm \alpha$$

where  $\alpha$  satisfies the equations

$$a = f \operatorname{cosech} \alpha \quad (4)$$

and

$$c = f \coth \alpha. \quad (5)$$

3. *Equal Cylinders with Equal Charges.*—The potential function  $\phi$  and the conjugate function  $\psi$  suggested for consideration are determined by the equation

$$\phi + i\psi = 4Q \log \{m \operatorname{sn}[(u + iv)K/\pi]\}, \quad (6)$$

in which  $Q$  is the charge per unit length of either cylinder,  $K$  is the real quarter-period of the elliptic function, and  $m$  is an arbitrary constant. The form of the function on the right is such that  $\phi$  is a periodic function of  $u$  with period  $2\pi$ . The condition that the potential  $\phi$  may be constant over the surfaces  $v = \pm \alpha$  is

$$K'/K = 2\alpha/\pi, \quad (7)$$

where  $2iK'$  is the imaginary period of the function  $\operatorname{sn}$ .

To prove this we have

$$\operatorname{sn}(z + iK') = \frac{1}{k \operatorname{sn} z},$$

and therefore

$$\operatorname{sn}^2\left(\frac{uK}{\pi} + \frac{iK'}{2}\right) = \frac{1}{k} \frac{\operatorname{sn}\left(\frac{uK}{\pi} + \frac{iK'}{2}\right)}{\operatorname{sn}\left(\frac{uK}{\pi} - \frac{iK'}{2}\right)},$$

so that, if (7) holds good, (6) gives when  $v = \alpha$

$$\phi = 2Q \log(m^2/k). \quad (8)$$

The function  $\phi$  has no poles in the finite part of the plane outside the cylinders, and as it has the same constant value over the two cylinders it represents the potential when they carry equal charges.

It is of interest to notice that  $e^{-2u} = q$ , where  $q$ , defined as  $e^{-u\pi/k}$ , is the quantity usually denoted by that letter in the theory of elliptic functions.

4. *Potential at a Great Distance (charges equal).*—The potential at a great distance from the conductors is determined by the asymptotic equation

$$\phi \sim 4Q \left[ \log \frac{2mKf}{\pi} - \log r \right], \quad (9)$$

where  $r$  is the radius vector from the origin.

If the zero of potential is on  $v = \alpha$ , it follows from (8) that  $m = k^{1/2}$ .

On this convention the potential at a great distance is given by

$$\phi \sim 4Q \left[ \log \frac{2k^{1/2}Kf}{\pi} - \log r \right], \quad (10)$$

and is therefore asymptotic to that due to a total charge  $2Q$  per unit length distributed over a cylinder of radius  $R$ , where

$$R = 2k^{1/2}Kf/\pi. \quad (11)$$

This equivalent radius is given in Table II.

Table I.—Dimensions.

$\text{Sin}^{-1} k$	$a$	$c/a = \cosh a$	$f/a = \sinh a$	$c/f = \coth a$
0	$\infty$	$\infty$	$\infty$	1
10	3.129	11.452	11.408	1.004
20	2.429	5.715	5.627	1.016
30	2.009	3.797	3.663	1.037
40	1.705	2.843	2.681	1.068
50	1.447	2.242	2.006	1.117
60	1.238	1.853	1.560	1.188
70	1.016	1.562	1.200	1.302
80	0.789	1.327	0.873	1.521
89	0.454	1.105	0.470	2.350
90	0	1	0	$\infty$

Table II.—Potential and Force.

$\text{Sin}^{-1} k$	$\gamma$	$\gamma + a$	$\gamma - a$	$R/a$	$\Delta$	$\Delta a/f$	$\Delta c/f$
0	$\infty$	$\infty$	0	$\infty$	1	0	1
10	3.128	6.262	0.004	4.79	0.992	0.087	0.996
20	2.428	4.872	0.014	3.39	0.970	0.172	0.985
30	2.044	4.063	0.035	2.78	0.932	0.254	0.968
40	1.769	3.474	0.064	2.42	0.879	0.331	0.940
50	1.544	2.991	0.097	2.16	0.814	0.406	0.909
60	1.380	2.608	0.152	1.99	0.733	0.470	0.871
70	1.236	2.262	0.220	1.85	0.630	0.525	0.821
80	1.106	1.998	0.317	1.74	0.510	0.584	0.776
89	0.672	1.426	0.518	1.63	0.301	0.642	0.709
90	0.908	0.908	0.908	1.57	0	0.667	0.667

5. *Distribution of Lines of Force, etc.*—To determine the distribution of the charge on either cylinder, a knowledge of the variation in  $\psi$  is necessary.

Equation (6) may be written

$$\phi + i\psi = 2Q \log [(m/k)^2 (ns \, 2w - ds \, 2w)(ns \, 2w - cs \, 2w)] \quad (12)$$

where

$$w \equiv (u + iv)K/\pi.$$

On writing  $v = \alpha = \pi K'/2K$  it is found that at points on the cylinder

$$\phi = 2Q \log m^2/k$$

as before, whilst

$$\psi = 2Q \left[ (2n+1)\pi - \tan^{-1} \left( \sec \frac{2uK}{\pi} \right) - \tan^{-1} \left( k \operatorname{sd} \frac{2uK}{\pi} \right) \right] \quad (13)$$

where  $n$  is an integer.

In passing round the cylinder  $u$  increases continually, and so does the first inverse tangent, but the second one oscillates about zero.

If we take  $n = 0$ , the formula gives

when  $u = 0$ ,  $\psi = 2Q\pi$ ; when  $u = \pi$ ,  $\psi = 0$ ; when  $u = 2\pi$ ,  $\psi = -2Q\pi$ .

6. *Density of the Charge.*—To find  $\sigma$ , the density of the charge, Equation 12 may be differentiated.

Since  $\sigma = -\frac{1}{4\pi} \frac{\partial \psi}{\partial n} \cdot \frac{\partial n}{\partial s}$ , where  $s$  is the arc on the circumference of the cylinder and  $\partial n$  is the element of the normal, it follows that

$$\sigma = \frac{K}{\pi^2} \frac{Q}{f} \left( \operatorname{dn} \frac{2uK}{\pi} + k \operatorname{cn} \frac{2uK}{\pi} \right) (\cosh \alpha - \cos u). \quad (14)$$

The mean surface density  $\bar{\sigma}$  is given by

$$\bar{\sigma} = Q/(2\pi a). \quad (15)$$

It follows that  $\sigma_0$ , the density at the points of either cylinder furthest from the other, and  $\sigma_1$ , the density at the points which are nearest, are related to  $\bar{\sigma}$  by the equations

$$\sigma_0 = \frac{2K}{\pi} (1+k) \tanh \frac{\alpha}{2} \cdot \bar{\sigma} \quad (16)$$

and

$$\sigma_1 = \frac{2K}{\pi} (1-k) \coth \frac{\alpha}{2} \cdot \bar{\sigma}, \quad (17)$$

respectively.

The ratio of these densities is given by

$$\sigma_0/\sigma_1 = \left\{ \tanh \frac{\alpha}{2} \tan \left( \frac{\pi}{4} + \frac{\theta}{2} \right) \right\}^2 \quad (18)$$

where  $\sin \theta = k$ .

The ratios  $\sigma_0/\bar{\sigma}$  and  $\sigma_1/\bar{\sigma}$  are tabulated in Table III. They are graphed as functions of  $c/a$  in fig. 1.

Table III.—Concentration of Charge.

$\sin^{-1} k$ .	Equal charges.		Opposite charges.		Only one cylinder charged.			
					Charged.		Uncharged.	
	$\sigma_0/\bar{\sigma}$ .	$\sigma_1/\bar{\sigma}$ .	$\sigma_0/\bar{\sigma}$ .	$\sigma_1/\bar{\sigma}$ .	$\sigma_0/\bar{\sigma}$ .	$\sigma_1/\bar{\sigma}$ .	$\sigma_1/\bar{\sigma}$ .	$\sigma_0/\bar{\sigma}$ .
0	1	1	1	1	1	1	0	0
10	1.084	0.909	0.916	1.091	1.000	1.000	-0.091	0.084
20	1.160	0.810	0.888	1.193	0.999	1.001	-0.192	0.161
30	1.229	0.703	0.768	1.309	0.996	1.006	-0.303	0.233
40	1.291	0.585	0.692	1.444	0.991	1.015	-0.430	0.300
50	1.347	0.466	0.619	1.616	0.983	1.041	-0.576	0.364
60	1.401	0.336	0.547	1.828	0.974	1.062	-0.746	0.427
70	1.449	0.205	0.468	2.135	0.958	1.170	-0.965	0.490
80	1.494	0.081	0.376	2.67	0.934	1.37	-1.30	0.560
89	1.545	0.002	0.223	4.48	0.884	2.24	-2.24	0.660
90	1.571	0	0	$\infty$	0.785	$\infty$	$-\infty$	0.785

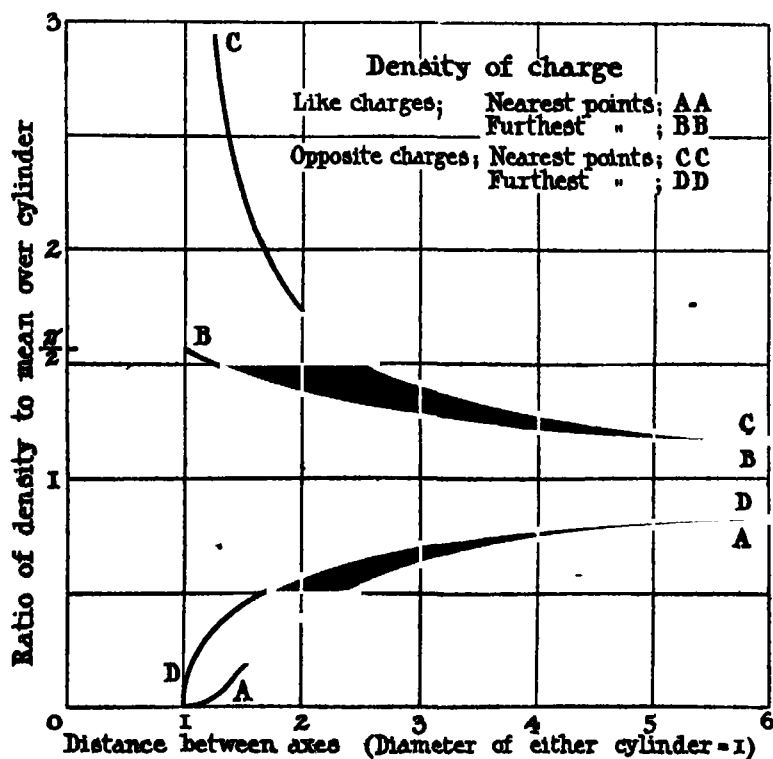


FIG. 1.—Surface densities at points on a common diameter of cylinders carrying equal charges. (Mean density over a cylinder unity.)

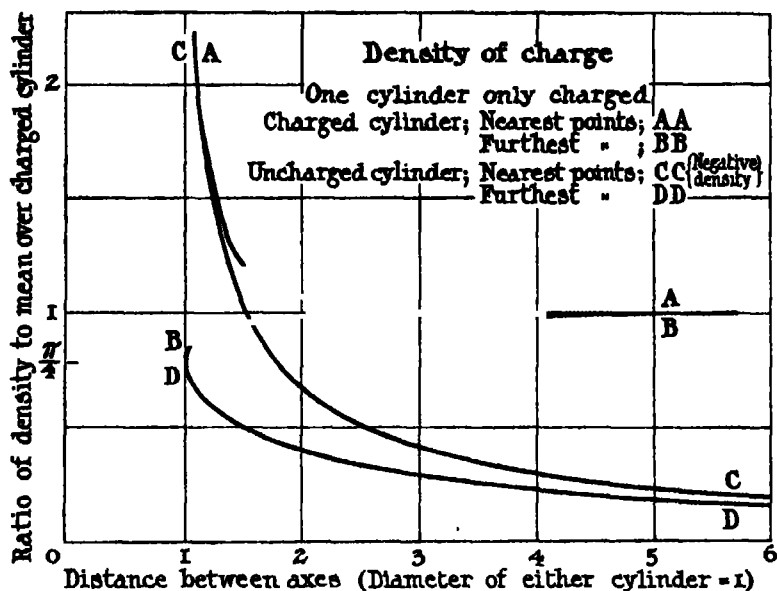


FIG. 2.—Surface densities at points on a common diameter of two cylinders, one charged, the other uncharged. (Mean density on charged cylinder unity.)

7. *Potential on the Axes.*—The way in which the potential  $\phi$  varies along the axes is of interest:—

(a) For  $u = 0$ , i.e., for the continuation of a common diameter of the cylinders, the equation (6) gives

$$\psi = 2Q\pi; \quad \phi = 4Q \log \{m \cdot \text{sc}'(vK/\pi)\}, \quad (19)$$

where the dash is to indicate that the complementary modulus  $K'$  is used.

(b) On the part of the common diameter intercepted between the cylinders  $u = \pi$ , and therefore

$$\psi = 0; \quad \phi = 4Q \log \{m \text{nd}'(vK/\pi)\}. \quad (20)$$

(c) On the axis of  $Y$ ,  $v = 0$ , and therefore

$$\psi = 0; \quad \phi = 4Q \log \{m \text{sn}(uK/\pi)\}. \quad (21)$$

8. *Potential on the Orthogonal Circle.*—As an additional guide for drawing the equipotentials and lines of force, their intersections with the circle, which cuts the conductors orthogonally and symmetrically, are required. The circle is specified by  $u = \pi/2$ .

Over this circle  $\phi$  and  $\psi$  are given by

$$\phi = 2Q \log \{m^2 / (\text{dn}'^2 vK/\pi + k' \text{cn}'^2 vK/\pi)\}, \quad (22)$$

and

$$\psi = 2Q [2\pi - \sin^{-1}(k' \text{sn}'^2 vK/\pi)],$$

which may be derived from (12).

9. *Repulsion between Cylinders Carrying Equal Charges.*—The repulsion per unit length is  $F$  where

$$F = 2\pi \int \sigma^2 \frac{dy}{ds} ds \quad (23)$$

the integral being taken round the circumference.

On substitution it is found that

$$F = \frac{4K^2Q^2}{\pi^2 f} \int_0^\pi \left( \operatorname{dn} \frac{2uK}{\pi} + k \operatorname{cn} \frac{2uK}{\pi} \right)^2 (\cosh \alpha \cos u - 1) du. \quad (24)$$

On integration this equation reduces to

$$F = AQ^2/f$$

where

$$A = 2 \left[ \coth \alpha - \left( \frac{2K}{\pi} \right)^2 \left( \frac{E}{K} - \frac{k'^2}{2} \right) \right], \quad (25)$$

$E$  being the second elliptic integral  $\int_0^K \operatorname{dn}^2 z \, dz$ .

The formula (25) has been used in computing the repulsion in Table II. The results are shown graphically in fig. 3.

It will be seen that for cylinders whose distance is large compared with their radii,

$$F \rightarrow Q^2/f.$$

On the other hand when the cylinders are very close

$$F \rightarrow 2Q^2/3a,$$

so that the repulsion between equal cylinders in contact carrying equal charges is the same as that between line charges at a distance equal to three radii, a result which can be verified by independent analysis of this important special case.\*

10. *Equal Cylinders; Any Charges.*—By combining the foregoing solution for equal positive charges with the well-known one for equal and opposite charges, viz.,  $\phi + \psi = -2\epsilon Q(u + v)$ , the distribution of potential in the general case can be found.

If the charges are  $Q_1$  on  $v = \alpha$  and  $Q_2$  on  $v = -\alpha$ , and if the zero of potential is at the origin, then

$$\phi + \psi = 2(Q_1 + Q_2) \log \operatorname{sn} \{ (u + v) K / \pi \} - \epsilon (Q_1 - Q_2) (u + v). \quad (26)$$

The potentials of the two cylinders are given by

$$\left. \begin{aligned} \phi_1 &= (Q_1 + Q_2) \log(1/k) + (Q_1 - Q_2) \alpha \\ \phi_2 &= (Q_1 + Q_2) \log(1/k) - (Q_1 - Q_2) \alpha \end{aligned} \right\}, \quad (27)$$

\* The solution depends on the equation

$$\phi + \psi = 4Q \log \tan \left( \frac{e^{-\epsilon \alpha}}{r} \cdot \frac{\pi}{2} \right).$$



whilst the potential at a great distance  $r$  is given by

$$\phi \sim 2(Q_1 + Q_2) \log \left( \frac{2K}{\pi} \cdot \frac{f}{r} \right). \quad (28)$$

The surface-density\* of the charge on the cylinder  $v = \alpha$  can be computed from the formula

$$\sigma = \left[ \frac{2K}{\pi} (Q_1 + Q_2) \left( \operatorname{dn} \frac{2uK}{\pi} + \operatorname{cn} \frac{2uK}{\pi} \right) + (Q_1 - Q_2) \right] \frac{\cosh \alpha - \cos u}{f}, \quad (29)$$

and the repulsion between the cylinders is determined by

$$F = \frac{A(Q_1 + Q_2)^2}{4f} - \frac{(Q_1 - Q_2)^2}{4f} \quad (30)$$

where  $A$  is defined by (25).

The force is negative, i.e., there is an attraction when  $Q_1 - Q_2$  is large compared with  $Q_1 + Q_2$ . The condition for the force to vanish is

$$\left( \frac{Q_1 - Q_2}{Q_1 + Q_2} \right)^2 = A. \quad (31)$$

When one of the cylinders is uncharged, so that  $Q_2 = 0$ , there is an attraction

$$-F = \frac{Q_1^2}{4f} [1 - A]. \quad (32)$$

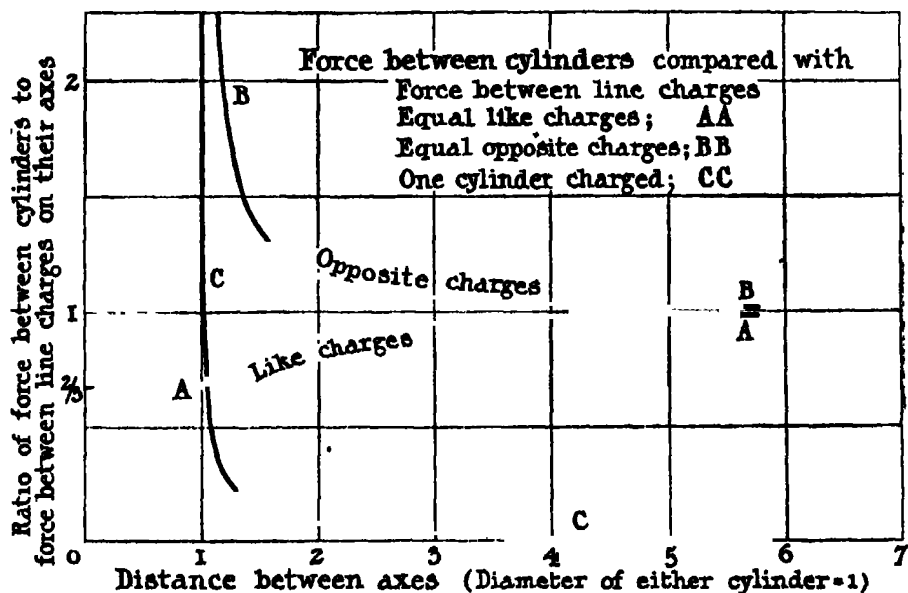


FIG. 3.—The force between two cylinders.

\* For the case  $Q_2 = 0$  the surface densities at the points where  $u = 0$  and  $u = \pi$  are tabulated in Table III and shown graphically in fig. 2.

11. *Potential and Capacity Coefficients.*—In the ordinary treatment of potential in three-dimensional problems, it is taken as zero at a great distance from the conductors under consideration. When dealing with cylinders which are regarded for the purpose of analysis as infinite, the difference of potential between them and an object at a great distance increases as the logarithm of the distance and this distance must appear explicitly in the formulæ.

In the present problem we are virtually compelled to complete our system of two cylinders with charges  $Q_1$  and  $Q_2$ , by supposing them to be surrounded by a very large cylinder, which may be supposed to have a radius  $r$ , and to be symmetrically placed with regard to them, and to have zero potential. It carries on its inner surface the charge  $-(Q_1 + Q_2)$ .

The potential of the first cylinder is now given by

$$\phi_1 = 2(Q_1 + Q_2) \log \left( \frac{1}{k^2} \frac{\pi}{2Kf} r \right) + (Q_1 - Q_2) \alpha, \quad (33)$$

so that if

$$\left. \begin{aligned} \phi_1 &= p_{11} Q_1 + p_{12} Q_2 \\ \phi_2 &= p_{21} Q_1 + p_{22} Q_2 \end{aligned} \right\} \quad (34)$$

we have

$$\left. \begin{aligned} p_{11} &= p_{22} = 2 \log(r/a) - (\gamma - \alpha) \\ p_{12} &= 2 \log(r/a) - (\gamma + \alpha) \end{aligned} \right\} \quad (35)$$

and

$$\gamma \text{ being written for } 2 \log \left( k^2 \frac{2Kf}{\pi a} \right), \quad (36)$$

or in the notation of § 4 for  $2 \log R/a$ .

Numerical values of the coefficients  $\gamma$ ,  $\gamma + \alpha$ ,  $\gamma - \alpha$ , are set out in Table II and shown graphically in fig. 4.

The charges can be written down in terms of the potentials in the form

$$\left. \begin{aligned} Q_1 &= K_{11} \phi_1 + K_{12} \phi_2 \\ Q_2 &= K_{12} \phi_1 + K_{11} \phi_2 \end{aligned} \right\}$$

where the capacity coefficients are given by the relations

$$\left. \begin{aligned} K_{11} &= K_{22} = \frac{2 \log r/a - (\gamma - \alpha)}{4\alpha \{2 \log r/a - \gamma\}} \\ K_{12} &= -\frac{2 \log r/a - (\gamma + \alpha)}{4\alpha \{2 \log r/a - \gamma\}} \end{aligned} \right\} \quad (37)$$

It will be noticed that as  $r \rightarrow \infty$  the capacity coefficients remain finite ;

$$K_{11} = K_{22} \rightarrow -K_{12} \rightarrow 1/4\alpha.$$

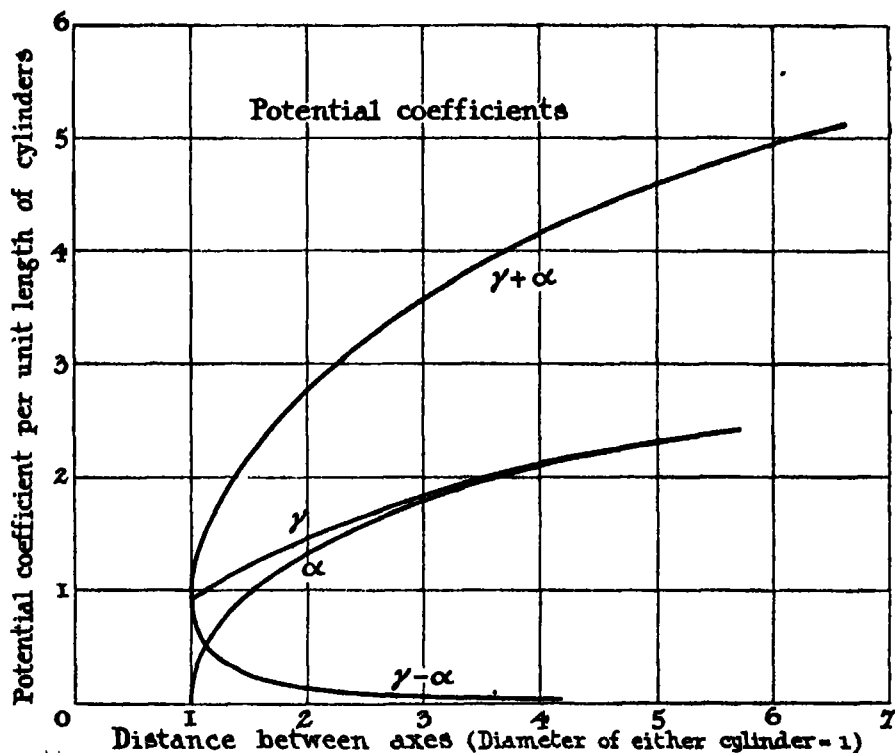


FIG. 4.—Potential coefficients.

These relations are not of direct service however: they merely indicate that, as long as  $(\phi_1 + \phi_2)/(\phi_1 - \phi_2)$  is small compared with  $\log r/a$ , the total charge on the two cylinders is negligible and that

$$Q_1 = -Q_2 = (\phi_1 - \phi_2)/4a \text{ approximately.}$$

It is of interest to compare the potential coefficient  $p_{11}$  with that of a single isolated cylinder of radius  $a$ , which is  $2 \log r/a$ . The difference  $2 \log r/a - p_{11}$  is equal to  $\gamma - \alpha$  and, therefore, independent of  $r$ . This indicates that bringing another conducting cylinder to the neighbourhood of a charged cylinder changes the potential of the latter by a finite amount. Calculation shows that as long as the distance is considerable the effect is small. When the gap between the cylinders is equal to the diameter of either, the difference is only 11 per cent. of its value when the gap is infinitesimal.

12. The electrostatic energy of the system per unit length is  $V$  where

$$\begin{aligned} V &= \frac{1}{2} (p_{11} Q_1^2 + 2p_{12} Q_1 Q_2 + p_{22} Q_2^2) \\ &= \frac{1}{2} [ \{ 2 \log r/a - \gamma \} (Q_1 + Q_2)^2 + \alpha (Q_1 - Q_2)^2 ]. \quad (38) \end{aligned}$$

Since  $\alpha \rightarrow 0$  as the cylinders are brought together it appears that there would be no loss of energy if they could be brought into contact without sparking. The bound charges are so close together on the two surfaces that their elimination when the two cylinders become a single conductor has no effect on the external field of force.

13. The space allotted to this paper does not permit of the application of the analysis to Russell's problem of the conductors carrying high-frequency currents. It may be mentioned, however, that the inductances required can be derived at once by the method developed in his discussion.

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**OBITUARY NOTICES**  
**OF**  
**FELLOWS DECEASED.**

## CONTENTS.

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	PAGE	
SIR WILLIAM CROOKES (with portrait) .....	i	
SIR JOSEPH WILSON SWAN .....	ix	207
GEORGE CARRY FOSTER .....	xv	







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*William Crookes.*

## SIR WILLIAM CROOKES, O.M., 1832—1919.

THE author of a succession of papers published by the Royal Society and other scientific bodies extending over 67 years (from 1851 to 1918), to say nothing of a number of technical treatises in the form of large volumes, must have been a man of remarkable industry as well as intellectual qualities, and those who believe in the influence of heredity will therefore be disposed to look for some indication of the ancestral origin of these qualities in the famous man who has so recently passed away.

His father, Joseph Crookes, born in 1792, the son of a small tailor in the north of England, came to London a poor boy. But he was evidently a man of brain and energy, for the tailor's business he established proved so prosperous, that when he died in 1884, at the age of 92, he was a rich man. Joseph Crookes married on February 24, 1831, at Aynhoe, Northamptonshire, as his second wife, Margaret Scott, and from this lady he had a second family of several sons and daughters. William was her firstborn, and resembling her in feature and in disposition, it may be surmised that he derived some of his characteristics from her.

There is but little to say concerning William Crookes's early years. Improbable as it may appear, he always maintained that he remembered learning to stand and to walk. Such regular education as he received was obtained at a grammar school at Chippenham. His father wished to make him an architect, but in the end he satisfied his inclination for experimental work, already indicated at home, by entering the Royal College of Chemistry under Hofmann, the first professor, in 1848. He must have made extraordinary progress, as in 1851 his first paper appeared in three German Chemical Journals to which it was communicated, doubtless by Hofmann. The English version was printed in the 'Quarterly Journal of the Chemical Society' (vol. 4, 1852), "On the Seleno-Cyanides, by William Crookes, Esq., Assistant in the Royal College of Chemistry." This position as Assistant he retained from 1850 to 1854. He then went to Oxford for a short time as Superintendent of the Meteorological Department at the Radcliffe Observatory, and in 1855 he became Lecturer on Chemistry at the Chester Training College.

In 1856 he married Miss Ellen Humphrey, a native of Darlington, whose acquaintance he had made some years earlier through school friends of his sister. They were married on April 10, 1856, at the Parish Church of St. Pancras, Middlesex, and began housekeeping at 20, Mornington Road, N.W. They removed to 7, Kensington Park Gardens in 1880, and this was their home to the end of their lives. In 1859 he brought out the first number of the 'Chemical News,' of which he remained sole editor till 1906.

In the meantime he seems to have been much occupied with the study of

phenomena connected with the nature and effects of light, for several papers relating to photography were published between 1853 and 1857. Soon after this the employment of the prism in recognising and distinguishing volatile substances in flame was introduced by Bunsen and Kirchhoff, and the discovery of rubidium and cesium in the water of the Dürkheim spring was announced by Bunsen in 1860. On applying the spectroscope to the seleniferous material from the vitriol works at Tilkerode (Harz), which had been given to him by Hofmann some years previously, and which he had used as the source of selenium in his work on the selenocyanides, Crookes observed a new green line which led him to the discovery of thallium. The first announcement of the existence of a new element appeared in the 'Chemical News,' March 30, 1861. It was originally supposed to be related to sulphur, but the discoverer soon saw fit to alter his opinion and the specimens exhibited in the International Exhibition, 1862, and to which a medal was awarded, were labelled Thallium, *a new metallic element*. The discovery was interesting from several points of view. The use of the spectroscope was novel and the properties of the new metal were strange, exhibiting as it does, the appearance and approximately the density of lead, some of its salts resembling those of lead and mercury, while others are perfectly similar in solubility and crystalline relations to the salts of the alkali metals. The discovery of thallium at once secured for William Crookes a recognised position in the scientific world, and in 1863 he was elected F.R.S. Obviously the first task which lay before him was the investigation of the chemical and physical properties of the new element and its sources in nature. Among the most important of the physical constants to be determined was the atomic weight, and the remarks on the subject contained in Prof. F. W. Clarke's "Constants of Nature" (Smithsonian Institution, 1882), may properly be quoted here. "In 1873, Crookes the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities of absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed specially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly *in vacuo*, but all were reduced to *absolute* standards, and unusually large quantities of thallium were employed in each experiment. . . . Suffice it to say that the research is a model which other chemists will do well to copy. . . . Hence, using the atomic weights and probable errors previously found for N and O,  $Tl = 203\cdot715 \pm 0\cdot365$ . If  $O = 16$ ,  $Tl = 204\cdot183$ . . . . Crookes himself, using 61\cdot889 as the molecular weight of the group  $NO_2$ , gets the value  $Tl = 203\cdot642$ ; the lowest value in the series being 203\cdot628 and the highest 203\cdot666, an extreme variation of 0\cdot038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes's work is concerned."

This passage illustrates the spirit which animated Crookes's work throughout. Nothing short of the highest attainable accuracy ever satisfied him.

The use of the vacuum balance, however, was attended by unexpected phenomena, which occupied his attention for many years afterwards and led to the discovery of the *radiometer* in 1875. This was described in a paper entitled "On Attraction and Repulsion resulting from Radiation," communicated to the Royal Society on March 20, 1875. A Royal Medal was awarded to Crookes at the Anniversary Meeting in the same year. The President in presenting the medal referred to the instrument in the form in which it has been since familiar, namely, with the four-armed fly mounted on a sharp point and having the vertical disks at the ends of the arms blackened on one side. He also remarked "it is the mystery attending this phenomenon that gives it its great importance." Great interest was manifested by many experimenters in the phenomena observed, and there were many attempts at explanation. In the end, the hypothesis put forward by Dr. G. Johnstone-Stoney, according to which the repulsion is due to the movements of the molecules of the residual gas acting differentially on the two surfaces of the movable disk, was accepted.

In a footnote to one of his papers ('Roy. Soc. Proc.,' vol. 25, p. 308, November 16, 1876), Crookes drew attention to the properties of highly attenuated gas, and expressed the view that the phenomena indicate the existence of a fourth state of matter as far removed from the condition of gas as gas is from liquid.

In all the numerous experiments connected with this investigation Crookes was assisted by Mr. C. H. Gunningham, whose mechanical dexterity and skill as a glass-blower were quite remarkable. Gunningham joined the Swan Electric Light Company in 1881, but unhappily died a few years later.

The phenomena exhibited by the electric discharge in rarefied gas had long been familiar and had been studied by Plücker, by Hittorf, and other physicists. It was natural that in the examination of the properties of highly attenuated gas the phenomena exhibited by electric discharge through such media should receive Crookes's attention, and in the paper in which his first experiments in this direction were described ('Roy. Soc. Proc.,' vol. 28, p. 110), he was led to theoretical speculations on the ultra gaseous state of matter. In this paper the dark space which appears round the negative pole was the subject of experiment and was found to enlarge as the exhaustion proceeds, while the phosphorescence excited on the glass walls of the tube diminishes and ultimately disappears. The dark region round the electrode has since been known as the *Crookes* or *cathode dark space*. The rays from the cathode may be made to converge by the use of an aluminium cup and the result is the production of a green phosphorescent spot on the glass, the rays travelling in straight lines cast a strong shadow from any object placed in their path. The rays when concentrated also develop great heat which may rise to the melting point of platinum.

In 1880 the French Académie des Sciences awarded Crookes an extraordinary prize of 3000 francs and a gold medal in recognition of his discoveries in molecular physics and radiant matter. In the years following

1880 he continued the active investigation of the phenomena exhibited by gases in a highly attenuated state, and among other properties he studied the heat conduction and viscosities of gases in this condition. He also examined the phosphorescence exhibited by many substances when exposed to the discharge from the negative pole in a highly exhausted tube; and in the Bakerian Lecture for 1883, speaking of this discharge as "radiant matter," he considered that the particles flying from the cathode were of the dimensions of molecules.

For some years he was occupied in tracing by the spectroscope the changes noted, and he was led to attempt the separation of some of the earths, notably yttria, into the components of which they were supposed to consist, by means of a very elaborate system of chemical fractionation. The result of all this work led him to speculations as to the characters of the elements and the existence of a class of bodies which he called "meta-elements." These meta-elements he regarded as composed of atoms "almost infinitely more like each other than they are to the atoms of any other approximating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight, which we ascribe to yttrium, therefore merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom we should find them varying within narrow limits on each side of the mean." This view was put forward in the Presidential Address to the Chemical Society, 1888, the whole of which even now after thirty years would repay perusal. The possibility of the evolution of the elements from a primal elementary protyl or urstoff is a proposition which has been discussed from the most ancient times, but the chemist had little positive information as to the interrelations among the recognised elements before the conception of the periodic law. Taking an idea from Prof. Emerson Reynolds for the diagrammatic display of the periodic relation of properties to atomic weight, Crookes produced a figure of eight curve, on which the symbols of the elements are placed at intervals so that the members of natural families fall into position vertically over one another.

On this curve the meta-elements would be ranged in groups or clusters close together. Radio-activity had not been discovered when this address was composed, but something approaching Crookes's idea has been realised in more recent times by the discovery of isotopes among the products of the disintegration of radio-active elements. For his researches on the behaviour of substances under the influence of the electric discharge in a high vacuum, with special reference to their spectroscopic behaviour, the Davy Medal was awarded to Crookes by the Royal Society in 1889.

The discovery of argon by Rayleigh and Ramsay in 1894, and of helium by Ramsay in 1895, opened a new field, and Crookes being recognised as the most experienced observer of spectra and the highest English authority in this direction, the new gases were at once submitted to him, and the

identity of terrestrial with solar helium was established finally by his examination.

Soon after this time the brilliant researches of J. J. Thomson threw an entirely new light on all the difficult spectroscopic questions which had been so patiently and so successfully examined by Crookes. It became clear that the particles projected from the cathode were much smaller than any known atoms or molecules of ordinary matter, and were in fact the minute bodies called electrons. On this point, Crookes in a paper on the "Stratifications of Hydrogen" (*Roy. Soc. Proc.*, vol. 79, p. 411), expressed himself in the following terms:—"In twenty-five years one's theories may change, although the facts on which they are based remain immovable. What I then called 'Radiant Matter' now passes as 'Electrons,' a term coined by Dr. Johnstone-Stoney to represent the separate units of electricity which is as atomic as matter. What was puzzling and unexplained on the 'Radiant Matter' theory is now precise and luminous on the 'Electron' theory." And by application of this theory the stratifications of hydrogen were explained.

The discovery of radio-activity by Henri Becquerel and of radium by Madame Curie towards the end of the century, naturally attracted Crookes's interest and attention. On examination of uranium salts some specimens were found to be much more radio-active than others. It was soon found that the radio-active constituent is precipitated from a solution by ammonia, and on adding excess of the reagent a small insoluble light brown precipitate is left which exhibits strong radio-active properties, while the uranium salt remaining is almost inactive. A year later the uranium had regained its activity. To the active substance the name Uranium X was given. Whatever be its nature, it is evident that uranium owes its usual activity to the presence of this substance which is generated from it and the separation of which depends on the readiness with which it attaches itself to precipitates, especially ferric hydroxide, when iron is present as an impurity in the uranium compound employed as material. The year following, Crookes continuing his observations on the emanations of radium, discovered the effects produced by the  $\alpha$  rays on a surface of hexagonal blende (zinc sulphide), and invented the little instrument, which he called the spinthariscopes, by which the number of scintillations can be counted, each spark being produced by one  $\alpha$  particle.

The researches on the spectra and other characters of the rare earths occupied more than 20 years, and one result was a very extensive study of scandium and its salts, which places it in the position of being now better known than almost any other of these difficult elements from which scandium is separated by its low atomic weight.

In 1908 Crookes drew attention to the remarkable resistance to the attack of all kinds of reagents by the metals iridium and rhodium, and in 1912 he recorded a useful series of observations on the relative volatility of metals of the platinum group. In the case of platinum at 1300° the metal seems to

volatilise *per se*, whereas the loss of weight of iridium is probably due to the formation of a volatile oxide. The spectra of elementary boron and silicon were the subjects of papers communicated to the Royal Society in 1912 and 1914.

A very valuable investigation undertaken in connection with the Glass Workers' Cataract Committee of the Royal Society, was begun in 1909. The main object was to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workpeople. This involved a study of the effects of the addition of a large number of metallic oxides to a colourless glass, specially prepared for the purpose by Mr. H. Powell of the Whitefriars Glass Works. The problem was to prepare a glass which would cut off as much as possible of the heat radiation, and at the same time be opaque to the ultra-violet rays, while the colour would be scarcely noticeable when used in spectacles. In the result, a series of 18 different recipes were provided which meet, more or less fully, the three requirements contemplated. These have been found to be, in practice, very beneficial to the workers.

We may now recall some of the subjects which at various times were studied by this untiring worker, outside the course of research which may be supposed to have represented his predilection.

It should not be forgotten that when quite a young man he was appointed by the Government to report on disinfectants and their application to the arrest of the cattle plague in 1866; and that he was responsible for the recognition of the antiseptic value of phenol or carbolic acid.

The diamond has been ever a subject of interest, not merely to the jeweller but to the mineralogist and chemist, owing to the mystery in which, up to recent times, its origin and formation were involved. In a visit to Kimberley in 1896, Crookes spent nearly a month in the mines studying the question of the origin of the mineral, and again in 1905, on the occasion of the visit of the British Association, he pursued the same enquiry. In 1893 the late Prof. Moissan demonstrated the production of diamonds by crystallisation of carbon from molten iron under pressure, and Crookes showed that the residue of cordite exploded in a closed steel cylinder contains crystalline particles possessing the form of the diamond. He published an interesting little book on Diamonds in 1909.

Another subject in connection with which he did good service was the importance of producing and applying to the land much larger quantities of nitrogen in the form of nitrate, in order to increase the supply of wheat. "The Wheat Problem" was one theme of his Presidential Address to the British Association at the meeting at Bristol in 1898, and his views on the subject were embodied in a volume published a year later, in which he was able to reply to the various critics who in the meantime had questioned some of his conclusions. Though doubtless some of his most startling statements admit of modification, the problem still remains a topic of supreme interest to the agriculturist and to the world at large.

It would be almost impossible to enumerate all the various directions in which Sir William Crookes (he received the honour of knighthood in 1897)

occupied himself in connection with problems of public interest or as expert adviser to the Government, but, in passing, may be mentioned his work on the disposal of town sewage, his Reports on the composition and quality of daily samples of the water supplied to London from 1880 to 1906, and his services as Consulting Expert on the Ordnance Board from 1907 onwards during the period of the war. Nor should it be forgotten that the office of President is in many learned societies no sinecure. In presiding over the Chemical Society (1887-1889), the Institution of Electrical Engineers (1890-1894), the British Association (1898), the Society of Chemical Industry (1913), and finally the Royal Society (1913-14-15), Sir William paid close attention to all the multifarious details of the business of each Society. He also served as Honorary Secretary to the Royal Institution from 1900 to 1913, and as Foreign Secretary to the Royal Society from 1908 to 1912. Every man of science among his contemporaries will be ready to affirm therefore that the numerous honours which were showered upon Crookes by the most distinguished Academies and Universities in the world were well earned and very fittingly conferred. He received from the Royal Society the Royal, the Davy, and the Copley Medals; and from the Royal Society of Arts the Albert Medal, and finally, in 1910, the Order of Merit was conferred upon him by the King.

Crookes's whole scientific career is interesting, apart from the value of his discoveries, as illustrating the fact that to a man of genius the character of his early education has but little influence on his achievements. As mentioned already, he left school at the early age of fifteen, and at once specialised in a single branch of science under a teacher eminent in his own line, but from whom the young student seems to have derived little but the advantage of example, for the subjects to which Hofmann devoted his energies appear to have had but little attraction for Crookes. Unlike W. H. Perkin, who also entered the College at about the age of fifteen with equally imperfect general education, he never seems to have been attracted by organic chemistry, and to the end of his life remained practically ignorant of this branch of science. But the genius displayed by Crookes was accompanied by unusual independence of character which was displayed in a variety of ways, not only in the course taken by his own researches, but by his attitude toward the statements and pretensions of others. Nothing seemed too improbable to escape his attention, and of this the time and trouble he was tempted to expend on the pretended transmutation of silver into gold some twenty years ago is a sufficient illustration. The same liberality of spirit made him very tolerant, and perhaps not always sufficiently critical in regard to articles in his paper, *'The Chemical News.'*

Here we must add that no account of William Crookes' life as a scientific man would be complete, and less than justice would be done to his personal character and independence of spirit if all reference were omitted to the investigations in which, early in his career, he became involved concerning the phenomena of so-called "Spiritualism." *'The Quarterly Journal of*



Science' for July, 1870, contains an article under the title, "Experimental Investigation of a New Force," in which Crookes describes experiments undertaken with Mr. D. D. Home, a "medium" well known to the public at that time. At one of the earlier *séances* the experiments were made in the presence of Dr. Huggins (afterwards Sir William Huggins, President of the Royal Society), Serjeant Cox, proprietor and conductor of the 'Law Times and Recorder of Portsmouth,' one of Crookes's brothers, and his chemical assistant. Later, in January, 1874, the same journal published "Notes of an Enquiry into the Phenomena called Spiritual during the years 1870-73," with the signature William Crookes.

Anyone who has read these articles can realise the shock which was experienced by the scientific world on learning the character of the statements contained in them. Here was a well-known man of science, a Fellow of the Royal Society, the discoverer of thallium, with which and with its salts, chemists had had time to become perfectly familiar, asserting in the most formal manner, that in his presence things had been seen and done which everyone would regard as contrary to well established natural law and to all ordinary experience.

It is perhaps not surprising that Crookes was publicly attacked in a violent manner, but he was able to show that many misrepresentations and mis-statements were made which everyone must now perceive were wholly unjustifiable. The story of his experiences as told by him is supported by evidence, which would be accepted as conclusive if these statements related to any scientific work or to any ordinary occurrence. Crookes himself never withdrew or altered his statements concerning the phenomena he had witnessed, and in his Presidential Address to the Meeting of the British Association at Bristol, so late as 1898, he reiterated his conviction as to their reality. This conviction he retained to the end of his life. He was President of the Society for Psychical Research in 1897. His view, if he really had a settled opinion, as to the explanation of these strange phenomena, cannot be given in his own words, but the view of Mr. Sergeant Cox on the theory of what he called psychic force, is given very clearly at the end of these "Notes," and it appears probable from the prominence given to this exposition, that it represents very nearly the opinion of Crookes himself. Perhaps the last few lines are sufficient to quote in this place, as probably views may have changed during the 45 years since they were written. The passage is as follows:—"The difference between the advocates of psychic force and the Spiritualists consists in this—that we contend that there is as yet insufficient proof of any other directing agent than the Intelligence of the Medium, and no proof whatever of the agency of the Spirits of the Dead; while the Spiritualists hold it as a faith, not demanding further proof, that the Spirits of the Dead are the sole agents in the production of all the phenomena. Thus the controversy resolves itself into a pure question of *fact*, only to be determined by a laborious and long continued series of experiments and an extensive collection of psychological facts."

It is unnecessary to pursue the subject further, but as Crookes made no secret of his views, and his credibility in regard to all other questions, scientific or otherwise, has never been impugned, his biographer would not be justified in doing more or less than to place on record such statements as appear to represent fairly the position he had assumed, and certainly no biographer would be expected to pronounce any opinion other than that which he believes to have been entertained by the subject of his notice.

By the death of Sir William Crookes on April 4, 1919, the world lost a great scientific pioneer. His age was far advanced, and the loss of his wife some two years earlier had been a severe blow, from which he never completely recovered, so that when in January last his friends learned of his increasing weakness, it was with the sad conviction that the end was not far off. The touching dedication prefixed to his little book on Diamonds was an indication of the domestic happiness which throughout accompanied his long and active career.

W. A. T.

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SIR JOSEPH WILSON SWAN, 1828—1914.\*

"THE earliest of my recollections relate to Pallion on the Wear near Sunderland, a notable place for shipbuilding when the only material used, or thought of, for shipbuilding was timber. Pallion was a small riverside place, with high banks, overlooking the river, and unspoiled country at the back, dotted with farms.

"Our house stood alone, with a large garden, overlooking the river, and upon the shipbuilding yards opposite and below.

"Along the fringe of the river there were a few other industries—lime-kilns and glass-works, a pottery, a paper-mill, and copperas works; and behind the river, farming still held sway, with here and there a large house with wooded grounds.

"I was only four years old when we left Pallion, but, still, memory has left some distinct traces of the things I saw and heard before we removed to Bishop Wearmouth, two miles away. . . . Our pleasant drawing-room is now included in the drawing office of the greatest firm of shipbuilders on the Wear."

\* At the request of the Council, the late Prof. Silvanus Thompson had undertaken to write the obituary notice of Sir J. W. Swan, when his unfortunate death prevented his completing the task. Miss Swan, with whom Prof. Thompson had been in communication, requested Dr. William Garnett to write a short account of her father's life. It is this account which is now published.—A. S.

Such is the description given by Sir Joseph Swan of the place of his birth as it appeared 90 years ago. As compared with Pallion to-day, the difference is as great as that between peace and war. Sir Joseph adds: "I very distinctly recall, on waking of a morning, the pleasant sound of the volleying blows of the mallets on the trenails, so different from, and so much more musical than, the harsher note that has since displaced it in connection with the modern iron ship.

"Before I was four I had visited all the works in the neighbourhood, been to the Glass House and seen the process of glass-blowing, . . . looked into the square pits of the copperas works, and very distinctly remembered the splendid appearance of the green crystals clinging to the sides; I had been in a pottery and seen clay thrown upon a wheel. . . . I had seen the limestone quarried and the process of lime-burning.

"I remember the flags and bands incidental to the election of 1832, just before we left Pallion."

At Bishop Wearmouth Joseph Swan attended a dame's school, where his principal achievements were in the direction of needlework, including the sampler, "with its border fantasy of branch and flower and yellow-throated nestlings of the nest." After a while he joined his brother John at Dr. Wood's school of about 200 boys, at Hendon Lodge, an old country mansion with extensive grounds. About two years after Joseph Swan's entrance, the school was removed to Hylton Castle, about 2 miles north of Sunderland, famous for its ghost—"The cauld lad of Hylton."

Joseph's uncle was the owner of a ropeworks, which had a gas plant of its own, and here the schoolboy had an opportunity of studying the manufacture and application of coal gas, but even then gas found in the boy's mind a powerful rival in electricity, for Mr. John Ridley, "a friend of the family," possessed an electric machine, with all the paraphernalia then usually associated with it. It was while the school was still at Hendon Lodge that Dr. Wood, the head-master, made the announcement: "Now, boys, if any of you want to write letters, I want to tell you that from to-morrow you can send a letter from one end of the country to the other—from Land's End to John o' Groat's house—all the way for a penny."

Joseph left school at the age of 12. Of his school books he remembered with special pleasure Hugo Reid's 'Chemistry' and Ewing's 'Elements of Elocution.' To the latter book he attributed much of his love for poetry and good literature. From the former he gained his first knowledge of Dalton's Atomic Theory and his first acquaintance with the manipulation of laboratory apparatus. In the autumn of 1842, after spending some time with his great-uncle, Commander Kirtly, R.N., he returned to Sunderland and was apprenticed to Hudson and Osbaldiston, druggists, for six years; but before three years had expired both partners were dead, and Swan joined his future brother-in-law, John Mawson, of Newcastle-upon-Tyne. This was the beginning of the firm of "Mawson and Swan," a partnership which was established in 1860. As an apprentice in Sunderland, Swan became a member of the local Athenæum

where he had access to scientific publications and popular lectures on Chemistry and Electricity. He says that it was from these lectures that he first became acquainted with the apparatus necessary for the production of electric light. Mr. W. E. Staite, the inventor of a regulating arc lamp, frequently lectured in Sunderland, exhibiting his lamp, which he recommended for light-house purposes, and in the course of his lectures he produced electric light from the incandescence of iridio-platinum wire. This set Swan thinking on the subject. He wanted to produce the same effect with a filament which would not fuse. Swan's special genius is well described in his own words respecting his experimental work in Chemistry and Electricity during his three years of apprenticeship in Sunderland: "I do not know whether it is a general experience or happy chance helping me, but somehow I have always been able to utilise in my experimental work things that happened to be well within my reach, and that seemed to offer themselves to me." Electrotyping, introduced to his notice by a neighbouring wood-turner, who used a flower-pot for a porous jar, soon attracted Swan's attention, and his work in this connection led him to study all the available forms of voltaic batteries, including the Callan and Bunsen batteries which Staite used for his electric light.

In those days it was not easy to obtain chemical apparatus in a provincial town, and Swan tells us how he extemporised gas jars out of Winchester quarts by means of a red-hot poker, and used Florence flasks for retorts. It was probably partly due to the difficulties which he thus experienced in Sunderland that he took an early opportunity of adding a department of chemical and physical apparatus to the pharmaceutical business in Newcastle. There was equal difficulty in securing materials for experimental work if they were not commonly used in pharmacy, and in his address to the students of the Pharmaceutical Society in 1903 Swan referred to the necessity of making for himself ammonium nitrate when he started on an investigation of the properties of nitrous oxide.

It was during these three years of apprenticeship that Swan first saw a Daguerreotype in an engraver's shop window in Sunderland. He says that involuntarily he associated the Daguerreotype with electrotyping, and then he saw in Bingham's '*Daguerreotype Manipulation*' a statement that Daguerreotypes could be reproduced in electrotypes. Referring to this period of invention, Swan says, "The elation created by the announcement of a great discovery and first acquaintance with its results is a sensation of an extraordinarily uplifting character, and I can never forget its effect as a stimulus to experimental effort."

On leaving Sunderland for Newcastle, Swan made the acquaintance of John Pattinson and Barnard Simpson Proctor, afterwards Professor of Pharmacy in Newcastle, and a nephew of Faraday. These three became known to their friends as "*The Three Philosophers*," as they held weekly meetings to discuss scientific questions. Between 1846 and 1859 Swan discussed electric lighting at the meeting of the three philosophers, and made experiments upon the carbonisation of parchmented and other paper heated

in charcoal powder in the biscuit kiln of a pottery. Swan was acquainted with the publication in 1845 of King's specification for producing electric light by means of continuous carbon conductors. He says, "*this was the first publication of the idea of an incandescent carbon lamp, with carbon in vacuo.*" Swan set to work to make the carbon conductor as thin as possible. He claimed that the idea of packing the paper or other material in powdered charcoal to exclude the air was original. The carbon from the parchmented paper had a metallic ring if allowed to fall on to a hard surface, and could be bent into the form of an arch. The resistance was so great that only short lengths could be made to incandesce with the battery power available, but a strip bent into the form of a horseshoe was maintained incandescent "for a considerable time" in an exhausted receiver. A strip of carbon about 0.25 inch wide bent into an arch 1.5 inches high was incandesced by means of 50 Callan cells. That early form of lamp was made in 1860. The great cost of current produced by primary batteries tended to discourage further experiment, as the lamp was not likely to be of practical service until the cost of current could be reduced. Swan accordingly, between 1862 and 1867, devoted much of his attention to photography, and investigated the nature of the effect of light upon bichromated paper and similar materials. He concluded that it consisted in the reduction of the chromic to the chromous salt, and that this formed an insoluble compound with the size of the paper. Fox-Talbot had used this reaction for photo-engraving. Swan saw in it the possibility of producing relief pictures, the surface corresponding to the lights and shades of silver prints—this was the germ of the carbon process, the Woodbury type and photogravure, and the investigation also had a bearing on the employment of chromous salt for tanning. The "Autotype" or "Carbon Process" was patented in 1864, and Swan's British patent was acquired by the Autotype Company.

One of the incidental results of the working out of the "Carbon Process" was the observation of the indurating effect of the salts of chromic oxide (of which chrome alum is a type) on gelatine. As a consequence of this observation, Mr. Swan proposed the application of the principle of this reaction to the leather-making industry. Chrome tanning, now an established industry, originated with this discovery.

In 1867 Mr. Mawson died, and the whole management of the business devolved for a few years upon Swan, so that he had little opportunity for continuing his scientific work until new partners were introduced into the business; but in 1877 his attention having been called to Dr. Maddox's experiments with bromide of silver used in conjunction with gelatine, in substitution for collodionized photographic plates, which furnished very uncertain results, he set to work to discover the cause of the irregularity. In his experimental researches with gelatino-bromide plates, Swan discovered the important fact that an immense increase of sensitiveness was caused in the emulsion by heating it during its preparation. He did not patent or publish his discovery, but applied it to the manufacture of dry plates,

thereby inaugurating a new era in photography. In 1879 he patented bromide printing paper.

In 1877 Swan learned that Mr. C. H. Stearn, of Birkenhead, had been working with high vacua, and he enlisted his services to carry out experiments with his carbon filaments. Swan hoped that in the higher vacua obtained by Stearn the filaments would last longer than in the receiver exhausted only by a piston pump. The difficulty then appeared of air occluded in the carbon and discharged when the filament was heated by the current. To meet this difficulty Swan raised the carbon to full incandescence while the process of exhaustion was continued, and then found that the vacuum was maintained when the lamp was incandesced after removal from the pump. Swan says, "our experiments were never conducted with great secrecy—especially we made no secret of the idea of constructing an electric lamp wholly of glass, platinum, and carbon," but on January 2, 1880, he patented the process of exhausting carbon lamps while in a state of incandescence. He adds, "I made no claim for any particular form of lamp, or for its being composed entirely of glass, carbon, and the platinum wires. I had debarred myself from making such a claim by the public exhibition of lamps having this feature more than a year previously. At a meeting of the Newcastle-upon-Tyne Chemical Society, held December 18, 1878, I showed an incandescent carbon lamp, which consisted wholly of a *glass bulb, pierced with two platinum wires, supporting between them a carbon filament.*" Swan lectured on electric lighting and exhibited his lamp before large audiences in the theatre of the Literary and Philosophical Society at Newcastle on February 3, 1879, and again in the Town Hall, Gateshead, on March 12 in the same year. In the following year the lecture room of the Literary and Philosophical Society in Newcastle was illuminated by a number of these lamps. Two events had contributed to the success of the lamp since Swan had showed his carbon horseshoe glowing in a mechanically-exhausted receiver. The Sprengel mercury pump had been invented in 1865, and the dynamo had enabled electric energy to be produced at a reasonable cost. The filament he subsequently employed was parchmented cotton thread carbonised. His production of the squirted collodion filaments followed soon after. The cellular lead plate for secondary batteries was another of Swan's contributions to electric lighting. The rapid deposition of copper by electrolysis occupied very much of his leisure 30 years ago, and he succeeded in depositing tough copper using a current density of 1000 amperes per square foot of cathode surface.

Sir Joseph Swan received the honour of knighthood in November, 1904. He was elected a Fellow of the Royal Society in 1894, and was made Chevalier of the Legion of Honour in 1881. He was President of the Institution of Electrical Engineers in 1898-9, and of the Society of Chemical Industry in 1900 and 1901. His death occurred at his home at Warlingham on May 27, 1914.

"For the important part he took in the invention of the electric lamp,

and for his invention of the carbon process of photographic printing," Sir Joseph Swan was awarded the Albert Medal of the Royal Society of Arts in 1906. The Hughes Medal of the Royal Society was awarded to him in 1904. He received the Gold Medal of the Society of Chemical Industry in 1903, and the "Progress" Medal of the Royal Photographic Society. He was the first President of the Faraday Society.

On March 4, 1914, the City Council of Newcastle-upon-Tyne resolved to present the Freedom of the City to Sir Joseph Swan "in recognition of his distinguished services in the cause of science, especially in the inventing and perfecting of incandescent electric lamps, and of rapid photographic dry plates." The actual presentation took place on July 9, a few weeks after Sir Joseph's death, when the family was represented by his son, Mr. Kenneth Swan, the ceremony having been postponed by the express wish of Sir Joseph, who hoped that summer weather would enable him to travel to Newcastle.

Of a charming personality and extremely social disposition, Sir Joseph Swan was always ready to share his good things with others. For his start on a scientific career he was largely indebted to the Popular Science lectures provided by the Sunderland Athenæum, and while he could give a highly technical address to a scientific society on the subjects which he had made his own, he was never happier than when he undertook an experimental lecture to a popular audience. In these lectures he avoided technicalities while giving such descriptions of inventions, processes, and apparatus as were calculated to inspire the younger members of his audience with the same zeal which had filled his own soul when a chemist's apprentice at Sunderland. On systematic scientific training he was equally keen. He took great interest in the development of the Armstrong College in its early days, and in his Presidential Address to the Society of Chemical Industry in Glasgow in 1901, he said, "A scientific training of University standard for our manufacturers and for our technical chiefs is an absolute necessity. Surely public money cannot be better spent than in providing adequate facilities for the educational equipment of the men of the future with this essential means of national defence. Our country possesses great stores of mineral wealth, a precious heritage that we are lavishly spending. That gift of nature will certainly not avert, and cannot go far to compensate for, the consequences of neglect of the scientific training to turn our fast-diminishing mineral wealth to the best advantage. One of the most pressing requirements of the moment . . . is *adequate endowment and encouragement of research.*"

W. G.

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## GEORGE CAREY FOSTER, 1835-1919.

GEORGE CAREY FOSTER was born at Saddington, in Lancashire, in 1835. His early education was at private schools, until he became a student in chemistry at University College, London, where he graduated in Honours. He was assistant for a time to Prof. A. W. Williamson, and left England in 1858 to study on the Continent, at Ghent, Paris, and Heidelberg. At Paris he studied under Kekulé, but gradually became more attracted to Physics, and several of the physical articles in 'Watts's Dictionary of Chemistry' are from his pen: notably the rather famous article "Heat," which appeared in 1863.

In 1862 he became Professor of Natural Philosophy in the Andersonian College, Glasgow; and in 1865 was elected to the Chair of Physics at University College, London, which he held till 1898. In 1900 he became Principal of the College for four years, an eventful period in the history of London University organisation.

The reconstruction of University College into the University of London, from which it never ought to have been separated, was an object very near his heart. It had begun near the beginning of the century, with high hopes and legitimate aspirations, and for a time it flourished as essentially the University of London. But a rival College was founded on more ecclesiastical lines; and, not being able to give a University Charter to both, wisdom decided that neither should have that dignity. An examining University was established by Government, apart from either teaching or research. And after that both Colleges led a struggling and parsimonious existence until recent times. Whether everything is now put right, those engaged in the work best know. From the advisory and administrative point of view, Foster did his best in a wise direction under exceptionally difficult circumstances.

Carey Foster's early publications were on chemical subjects. They appear in the 'British Association Reports' for 1857 and 1859, when he reviewed recent progress in Organic Chemistry. In 1860, while at Ghent, he described an isomer of hippuric acid; and in 1861 published a paper "On Piperic and Hydropiperic Acids." Several more important papers he published in association with Matthiessen, mainly on the constitution of narcotine and on the production of a new compound called cotarnic acid.

Says Dr. Forster Morley:—"These three papers by Foster and Matthiessen made a long step forward in the knowledge of the constitution of the alkaloids, and may, indeed, be termed classical. The accuracy of the work has been amply confirmed by subsequent investigation." And, he adds: "Carey Foster's work in chemistry shows that, if he had decided to devote himself to that science, he would have taken a distinguished position among his colleagues."

Undoubtedly, however, Carey Foster's best known and perhaps most



important scientific work was connected with the employment of the Wheatstone bridge for purpose of accurate measurement and for comparison of standards of electrical resistance. So much so, that his modification of it is specially constructed for that purpose, and known as the Carey Foster bridge. His ingenious though simple paper on the subject will be found in the 'Journal of the Society of Telegraph Engineers' for 1872-1873, vol. 1, p. 196. His treatment of it is worth reading, for his neat obtaining of the difference-formula is by no means obvious. Dr. Glazebrook invariably used the Carey Foster method during his custody of, and most careful watch for variations in, the coils which were the National standards of resistance for many years.

Carey Foster applied the same principle to determine the resistance of any good conductor. Quite short thick pieces of metal could be dealt with, and it was in this way that the present writer determined the conductivity of sundry copper-tin alloys ('Phil. Mag.,' December, 1879, p. 554), detecting a curious anomaly which had been previously missed. It was, in fact, an anticipation of the potentiometer method, and Carey Foster was able to plot equipotential surfaces with much greater ease and accuracy than had previously been achieved, either on the Continent or anywhere. The simplicity and effectiveness of his device for plotting the curves of currents flowing in various shapes of tinfoil, with differently situated electrodes, could not be excelled.

Some papers on the Flow of Electricity in a Plane, by himself and the present writer, may be here referred to. They represent a good deal of work, and were perhaps Foster's most ambitious publication ('Phil. Mag.' for May, June, and December, 1875, vols. 49 and 50, pp. 385, 453, and 475). It was gradually found that a good deal of theoretical work in this connection had been done by Kirchhoff and by Prof. W. Robertson Smith. (For an extension, see 'Phil. Mag.,' Ser. V, vol. 1, 1876.)

Foster was always an important member of the British Association Committee on Electric Standards, often occupying the chair at its meetings; and later he made a series of experiments on absolute determinations of resistance, in conjunction with G. W. de Tunzelmann. In 1886 he devised a method of determining a coefficient of mutual induction by comparing it with the capacity of a condenser, and so arranging that the galvanometer deflection to be observed was annulled. It is a method which allows of high accuracy.

The writer, as a student under Carey Foster's instruction, investigated, for a British Association Committee, the Siemens' electric pyrometer, and drew attention to the slight changes which its main wire underwent after heating, apparently by reason of the effect of hot gases penetrating the iron sheath and getting at the platinum. The writer was impressed with the consummate care and scrupulous accuracy demanded by the Professor in this comparatively simple research.

In conjunction with Dr. Fison, Foster determined the potential needed to

give sparks in air, using a specially designed form of absolute electrometer, and in conjunction with Dr. A. W. Porter, he published a well-known textbook on Electricity. He was president of Section A of the British Association in 1877, and in his address dwelt on the importance of accurate measurement as the foundation of discovery in science. He also half-humorously supported the idea that a physical theory could not be regarded as complete until it could be expounded to any intelligent man—"at least, if he was not in a hurry to catch a train."

The Physical Society of London, now a flourishing organisation, owes its origin largely to Carey Foster, working in association with one who was still more its founder, Prof. Frederick Guthrie. The two were in frequent consultation in and before the year 1873, and at a later stage both held the office of President in due course. Foster was also President of the Society of Telegraph Engineers. His fellowship of the Royal Society dates as far back as 1869, and he was twice elected a Vice-President. Glasgow and Manchester conferred upon him their honorary doctorates.

The above is a bald and brief summary of salient facts in a life which was quiet and unobtrusive, but the enthusiasm of many of his distinguished students is not explicable by any such bare recital. The language of exaggeration was always repulsive to him, but that he was everywhere regarded with sincere affection by those who knew him is nothing more than simple fact.

Was he a good teacher? That depends on the point of view. He was not a good lecturer; he was far from fluent, and he was so conscientious about expressing himself correctly that sometimes he failed to express himself at all. But if his halting words were taken down as uttered, they were invariably accurate and sensible and couched in good English. In writing he was slow and painstaking. So he was in speaking. Accordingly, it was only an instinctive sense of respect for a learned and courteous gentleman that kept a large and junior class in order. The bulk of them could not really know him, and yet they appreciated him. By his senior students he was both known and beloved. His manner was, to them, no deterrent; they recognised beneath it a solid reality, devoid of all show and pretence, but wise, judicious, careful, and trustworthy.

His judgment was astonishingly sound; his opinion was frequently asked on many topics, and very seldom was he misled into giving a wrong one. He might err on the side of caution, but when he held opinions he held them strongly, and the reticence with which he expressed his views caused them to be received with the more attention. Never was anyone more conspicuously free from self-seeking, and people knew it.

So the fact is that Foster was a genuine and very real, though very modest, teacher. He would discuss problems on equal terms with members of his class, spending any amount of time after a lecture, and he was working with the students in his laboratory every day. Indeed, the physical laboratory at

University College was his creation, out of a couple of preparation rooms. During his early tenure of the chair there appears to have been no students' physical laboratory south of the Tweed. Gradually the laboratory began, in a very small way, at first for senior students only, but afterwards for all who were ready to come; and University College has done well to call its later well-equipped new building "The Carey Foster Laboratory."

A fuller and more detailed obituary notice, by his friend and old student, Dr. A. H. Fison, may be referred to in the 'Transactions of the Chemical Society' for 1919, vol. 115, pp. 412—427.

In his domestic life Foster was exceptionally happy; his eight children are all living, and his wife only predeceased him by 18 months. He died at Rickmansworth on February 9th, 1919, aged 84.

To the writer during his early struggles in London he held out a helping hand, as he doubtless did also to many an ambitious and impecunious student. He leaves behind a fragrant memory, for he was one of the best and most unselfish of men.

O. J. L.

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# INDEX to VOL. XCVI. (A)

- Address of the President, December 1, 1919, 311.
- Adsorption of gases—theoretical adsorption isostere and isotherm, experimental verification (Williams), 287, 289, 298.
- Airey (J. R.) Zonal Harmonics of High Order in Terms of Bessel Functions, 1.
- Algebra, linear associative, suitable for electromagnetic relations and relativity theory (Johnston), 331.
- Archbutt (S. L.) See Rosenhain and Archbutt.
- Area of surfaces (Young), 71.
- Armstrong (E. F.) and Hilditch (T. P.) A Study of Catalytic Actions at Solid Surfaces. I.—Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel, 137; II.—The Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel, 322.
- Aston (F. W.) Experiments with Perforated Electrodes on the Nature of the Discharge in Gases at Low Pressures, 200.
- Atmospheric Stirring measured by Precipitation (Richardson), 9.
- Ayrton (H.) On a New Method of Driving off Poisonous Gases, 249.
- Bairato (G. E.) On the Variation with Frequency of the Conductivity and Dielectric Constant of Dielectrics for High-frequency Oscillations, 363.
- Bakerian Lecture (Strutt), 272.
- Balmer series, intensity decrement in (Merton and Nicholson), 112.
- Bessel functions, zonal harmonics in terms of (Airey), 1.
- Biotite, transparency of, to infra-red radiations (Martin), 185.
- Bone (W. A.) and Sarjant (R. J.) Researches on the Chemistry of Coal. Part I.—The Action of Pyridine upon the Coal Substance, 119.
- Brown (E. W.) On the Determination of the Secular Acceleration of the Moon's Longitude from Modern Observations, 69.
- Cantilevers, solution for flexure of, and influence of manner of fixing the built-in end (Seegar and Pearson), 211.
- Catalytic actions at solid surfaces. II.—Hydrogenation of unsaturated fats in presence of nickel (Armstrong and Hilditch), 137, 322.
- Chapman (S.) A Note on Dr. Chree's Recent Discussion of Two Magnetic Storms, 424.
- Chree (C.) Magnetic Storms of March 7-8 and August 15-16, 1918, and their Discussion, 32; — An Explanation of Criticisms on Dr. S. Chapman's Recent Paper "An Outline of a Theory of Magnetic Storms," 420.
- Clouds, measurement of water in (Richardson), 19.
- Coal, chemistry of. I.—Action of pyridine on coal substance (Bone and Sarjant), 119.
- Conductors, parallel cylindrical, in electrical problems (Whipple), 465.
- Crookes (Sir W.) Obituary notice of, i.
- Curtis (W. E.) The Value of the Rydberg Constant for Spectral Series, 147.
- Dielectrics, variation with frequency of conductivity of, for high-frequencies (Bairato), 363.
- Diffracting boundaries, radiation from laminar (Ghosh), 257.
- Discharge in gases at low pressures, experiments on nature of (Aston), 200.
- Eccles (W. H.) and Vincent (J. H.) On the Variations of Wave-length of the Oscillations generated by Three-electrode Thermionic Tubes due to Changes in Filament Current, Plate Voltage, Grid Voltage, or Coupling, 455.

- Electrical problems, equal parallel cylindrical conductors in (Whipple), 465.  
 Electron ring theory of atoms (Schott), 395.  
 Electrons, scattering of X- and  $\gamma$ -Rays by rings of (Schott), 395.
- Flexure of cantilevers of certain cross-sections, de Saint-Venant solution for (Seegar and Pearson), 211.
- Foster (G. C.) Obituary notice of, xv.
- Garnett (J. C. M.) On certain Independent Factors in Mental Measurements, 91.
- Gases, adsorption at low and moderate concentrations (Williams), 287, 289, 298.
- Gases, new method of driving off poisonous (Ayrton), 249.
- Ghosh (P. N.) On the Colours of the Striae in Mica, and the Radiation from Laminar Diffracting Boundaries, 257.
- Hilditch (T. P.) See Armstrong and Hilditch.
- Hydrogen, secondary spectrum of (Merton), 382.
- Hydrogenation of unsaturated fats in presence of nickel (Armstrong and Hilditch), 137, 322.
- Isotopes, spectra of (Merton), 388.
- Jeffreys (H.) On the Relation between Wind and Distribution of Pressure, 233.
- Johnston (W. J.) A Linear Associative Algebra suitable for Electromagnetic Relations and the Theory of Relativity, 331.
- Larmor (Sir J.) On Generalized Relativity in connection with Mr. W. J. Johnston's Symbolic Calculus, 334.
- Light, diffusion by rain, cloud, or fog (Mallock), 267.
- Magnetic Storms of 1918 and their discussion (Chree), 32 ; (Chapman), 424 ; (Chree), 426.
- Magnetic susceptibilities of low order, measurement of (Wilson), 429.
- Mallock (A.) Diffusion of Light by Rain, Cloud, or Fog, 267.
- Martin (L. C.) The Transparency of Biotite to Infra-red Radiations, 185.
- Medals, presentation of, 318.
- Mental measurements, independent factors in (Garnett), 91.
- Merton (T. R.) On the Secondary Spectrum of Hydrogen, 382 ; — On the Spectra of Isotopes, 388 ; — and Nicholson (J. W.) Note on the Intensity Decrement in the Balmer Series, 112.
- Metals, inter-crystalline fracture of, under prolonged stress (Rosenhain and Archbutt), 55.
- Moon's longitude, determination of secular acceleration (Brown), 69.
- Nicholson (J. W.) See Merton and Nicholson.
- Obituary Notices :—Crookes, Sir W., i ; Swan, Sir J. W., ix ; Foster, G. C., xv.
- Oscillations generated by three-electrode thermionic tubes, variations of wave-length of (Eccles and Vincent), 455.
- President's Address, December 1, 1919, 311.
- Rain, cloud, or fog, diffusion of light by (Mallock), 267.
- Relativity, an associative algebra suitable for theory of (Johnston), 331 ; — generalized, in connection with Johnston's calculus (Larmor), 334.
- Richardson (L. F.) Atmospheric Stirring measured by Precipitation, 9 ; — Measurement of Water in Clouds, 19.

- Rosenhain (W.) and Archbutt (S. L.) On the Inter-crystalline Fracture of Metals under Prolonged Application of Stress (Preliminary Paper), 55.
- Rydberg constant, value of, for spectral series (Curtis), 147.
- Sarjant (R. J.) See Bone and Sarjant.
- Schott (G. A.) The Scattering of X- and  $\gamma$ -Rays by Rings of Electrons—a Crucial Test of the Electron Ring Theory of Atoms, 395.
- Seegar (M.) and Pearson (K.) De Saint-Venant Solution for the Flexure of Cantilevers of Cross-Section in the form of Complete and Curtate Circular Sectors, etc., 211.
- Selenates, double, of cobalt group (Tutton), 156.
- Sodium, line spectrum of, excited by fluorescence (Strutt), 272.
- Spectra of Isotopes (Merton), 388.
- Spectral series, value of Rydberg constant for (Curtis), 147.
- Spectrum of hydrogen, secondary (Merton), 382; — of sodium as excited by fluorescence (Strutt), 272.
- Striae in mica, colours of (Ghosh), 257.
- Strutt (Hon. R. J.) Bakerian Lecture: A Study of the Line Spectrum of Sodium as excited by Fluorescence, 272.
- Swan (Sir J. W.) Obituary notice of, ix.
- Taylor (G. S.) Tidal Friction in Irish Sea, 330.
- Thomson (Sir J. J.) Anniversary Address, December 1, 1919, 311.
- Tidal Friction in Irish Sea (Taylor), 330.
- Tutton (A. E. H.) Monoclinic Double Selenates of the Cobalt Group, 156.
- Variables in multiple integral, change of independent (Young), 82.
- Vincent (J. H.) See Eccles and Vincent.
- Whipple (F. J. W.) Equal Parallel Cylindrical Conductors in Electrical Problems, 465.
- Williams (A. M.) The Adsorption of Gases at Low and Moderate Concentrations.—Part I, 287; Part II, 289; Part III, 298.
- Wilson (E.) The Measurement of Magnetic Susceptibilities of Lower Order, 429.
- Wind and pressure distribution, relation between (Jeffreys), 233.
- X- and  $\gamma$ -Rays, scattering by rings of electrons (Schott), 395.
- Young (W. H.) On the Area of Surfaces, 71; — On Change of the Independent Variables in a Multiple Integral, 82.
- Zonal Harmonics in terms of Bessel Functions (Airey), 1.

END OF THE NINETY-SIXTH VOLUME (SERIES A).



